# New process for reduction of polluting emissions in livestock buildings

<u>B. Delgado</u><sup>\*1,2,3</sup>, L. Retailleau<sup>3</sup>, S. Godbout<sup>1</sup>, R. Lagace<sup>2</sup>, A. Avalos Ramirez<sup>4</sup>, A. Giroir-Fendler<sup>3</sup>

<sup>1</sup>Institut de recherche et de développement en agroenvironnement, 2700 rue Einstein, Québec (QC) G1P 3W8 Canada.

<sup>2</sup>Département des Sols, Université Laval, 2425 rue de l'agriculture, Québec (QC) GIV 0A6 Canada.
<sup>3</sup>Université de Lyon, Lyon, F-69003, France, Université Lyon 1, Villeurbanne, F-69622, CNRS, UMR 5256 IRCELYON, 2 avenue Albert Einstein, Villeurbanne, F-69622, France.
<sup>4</sup>Centre National en Électrochimie et en Technologies Environnematoles, 2263 avenue du Collège Shawinigan (QC) G9N 6V8 Canada.
\*corresponding author:beatriz,delgado@irda.gc.ca

## Introduction

It is of prime importance to reduce the emissions of methane (CH4) and nitrous oxide ( $N_2O$ ), whether they emanate from stationary sources such as livestock buildings. There are several methods for eliminating air pollutants, which can be grouped into two main categories. One category comprises separation-and-recovery techniques such as absorption or adsorption, and the other category comprises the so-called destruction techniques such as catalytic combustion or decompositon. These latter techniques are more effective when the pollutants are present in trace amounts, but this requires the use of heterogeneous catalysts.

In livestock buildings, the concentration of  $N_2O$  and  $CH_4$  emitted is not constant during the day or over the seasons [1]. To achieve the pollutants abatement, a process constituted by an adsorption step followed by a catalytic treatment is proposed. The adsorption unit will be capable of trapping efficiently and selectively  $N_2O$  and  $CH_4$ , whereas the catalytic system will be an oxidation or decomposition process.

The aim of this project is to develop a simple and economical technology to treat catalytically  $N_2O$  and  $CH_4$  emissions issued from farm buildings used for intensive livestock breeding, such as diary cattle.

#### Materials and Methods

As an initial step, simple and well-identified supports are tested in order to measure the adsorption capacity for  $N_2O$  and  $CH_4$ . Special emphasis is placed on estimating the competitions for adsorption among the molecules that are present in the real exhaust gases issued from livestock buildings, such as water vapor, carbon dioxide, and ammonia. Innovative materials prepared using mixtures of several adsorbents are developed and hydrothermal syntheses are preferred in order to obtain systems of homogeneous composition. The desorption temperature of catalyst supports were measured using the methods of temperature programmed desorption (TPD).

The breakthrough curves will allow determining the physical and kinetic parameters of the catalyst support. The total flow rates of gases, the temperature of catalytic unit, and the mass of adsorbents and catalysts are operating parameters that affect the global efficiency of the adsorption-reaction system and they will be used to compare the performance of materials.

The catalysts commonly used for  $CH_4$  combustion and decomposition of  $N_2O$  are shown in Table 1. The Ag/ZSM5 and Ag/Al<sub>2</sub>O<sub>3</sub> catalysts were selected for the catalytic treatment of  $CH_4$  and  $N_2O$ . They were prepared using the impregnation method or

hydrothermal exchange. The crystal structure of catalysts was determined with X-ray powder diffraction (XRD). The BET surface areas were measured by  $N_2$  adsorption at 77°K and the content of silver was defined by ICP analysis.

Table 1. Catalysts for CH<sub>4</sub> combustion and N<sub>2</sub>O selective reduction.

	Method	Catalyst	T (°C)	Ref
CH <sub>4</sub>	Impregnation	Pd / Al <sub>2</sub> O <sub>3</sub>	473-873	[2]
	Impregnation	Cr / Ce / Al <sub>2</sub> O <sub>3</sub>	300-480	[3]
	Co-precipitation	Cr / Co	300-650	[4]
	Citrate sol-gel	La2CuNiO6	400-700	[5]
	Impregnation	Ag / ZSM5	300-700	[6]
$N_2O$	Citrate sol-gel	LaCo <sub>1-x</sub> Fe <sub>x</sub> O <sub>3</sub>	100-900	[7]
	Impregnation	Ag / ZSM5	200-700	[6,8]
	Impregnation	Fe / ZSM5	275-375	[9,10]

The reduction and oxidation properties of catalysts were measured using the methods of temperature programmed reduction (TPR) and temperature programmed oxidation (TPO). Catalytic tests were performed for  $CH_4$  oxidation and  $N_2O$  decomposition in a fixed bed reactor. A stream consisting of 100 ppmv of  $CH_4$ , 20 ppmv of  $N_2O$  and helium balance at a total flow rate of 100 ml/min was passed through the catalyst bed.

#### Conclusion

In this study, the influence of various parameters on the adsorption capacities like the nature of the adsorbent, the presence of water,  $CO_2$  and ammonia content in the gas stream are presented. Furthermore, we proposed and evaluated the integration of a desorption step followed by a catalytic phase for the abatement of  $CH_4$  and  $N_2O$  in a synthetic gas effluent. We observed that the combination of adsorption-desorption and catalytic decomposition processes could be an interesting solution to treat greenhouse gases present in exhaust air.

## References

[1] A. Costa, M. Guarino. Atmospheric Environment 2009, 43, 1548.

[2] S. Yang, A. Maroto-Valiente, M. Benito-Gonzalez, I. Rodriguez-Ramos, A. Guerrero-Ruiz. Applied Catalysis B: Environmental 2000, 28, 223.

[3] X. Yuan, S. Chen, H. Chen, Y. Zhang. Catalysis Communications 2013, 35, 36.

[4] J. Chen, X. Zhang, H. Arandiyan, Y. Peng, H. Chang, J. Li. Catalysis Today 2013, 201, 12.

[5] R. Hu, R. Ding, J. Chen, J. Hu, Y. Zhang. Catalysis Communications 2012, 21, 38.

[6] C. Shi, M. Cheng, Z. Qu, X. Bao. Applied Catalysis B: Environmental 2004, 51, 171.

[7] Y. Wu, C. Cordier, E. Berrier, N. Nuns, C. Dujardin, P. Granger. Applied Catalysis B: Environmental 2013, 140, 151.

[8] F. Schuricht, W. Reschetilowski. Microporous and Mesoporous Materials 2012, 164, 135.[9] X. Cheng, X.T. Bi. Chemical Engineering Journal 2012, 211, 453.

[10] T.T. Yang, H.T. Bi, X. Cheng. Applied Catalysis B: Environmental 2011, 102, 163.