Journal of Catalysis 328 (2015) 236–247

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Catalytic abatement of NO and N_2O from nitric acid plants: A novel approach using noble metal-modified perovskites

Y. Wu[a], C. Dujardin[a], C. Lancelot[a], J.P. Dacquin[a], V.I. Parvulescu[b,*], M. Cabié[c,d], C.R. Henry[c], T. Neisius[d], P. Granger[a,*]

[a] Unité de Catalyse et de Chimie du Solide UMR 8181, Université Lille1 Sciences and Technologies, Cité scientifique, bâtiment C3, 59650 Villeneuve d'Ascq, France
[b] University of Bucharest, Faculty of Chemistry, Department of Organic Chemistry, Biochemistry and Catalysis, 4 – 12 Regina Elisabeta Bvd., Bucharest 030016, Romania
[c] Centre Interdisciplinaire de Nanoscience de Marseille, CNRS UPR 3118, Associated to Aix-Marseille Université, Campus Luminy, 13288 Marseille, France
[d] Fédération des Sciences Chimiques de Marseille, Aix Marseille Université, 13397 Marseille Cedex 20, France

ARTICLE INFO

Article history:
Received 4 September 2014
Revised 27 January 2015
Accepted 5 February 2015

Dedicated to the memory of Haldor Topsøe.

Keywords:
Catalytic N_2O decomposition
NO/H_2 reaction
Nitric acid nitric plant
Precious metals
Perovskite

ABSTRACT

A combined study was achieved to remove sequentially trace amounts of N_2O and NO from nitric acid plants. Catalytic systems involving perovskite-type materials have been developed in which precious metals were incorporated in order to compensate deactivation processes for high-temperature N_2O decomposition and to enhance the usual low-temperature activity in NO conversion. The high-temperature catalytic decomposition of N_2O was studied in the temperature range 500–700 °C in realistic conditions with 1000 ppm N_2O, 5000 ppm NO, 6 vol.% $O_{2,}$ and 15% H_2O. Starting from $LaC_{0.95}Pd_{0.05}O_3$ prepared by a sol gel route, it was found that appropriate sequential oxidative/reductive pre-activation thermal treatments can lead to the diffusion and the segregation of PdO_x clusters in strong interaction with the perovskite structure. A sharp increase in intrinsic rates and an apparent compensation effect emphasize the importance of the PdO_x-support interface where Pd at the vicinity of anionic oxygen species from the perovskite can facilitate the formation of anionic vacancies potentially active for N_2O dissociation. Regarding the NO/H_2 reaction, Pt supported on $LaFeO_3$ shows remarkable activities below 100 °C depending on the temperature of the pre-reductive thermal treatment and the aging process at 500 °C in reaction conditions. Activity in NO reduction at 80 °C has been explained from the involvement of the Pt–$LaFeO_3$ interface supported by HRTEM observations relative to the growth of epitaxially orientated Pt particles and the correlation observed between calculated rates based on the length of the interfacial perimeter increasing with the particle size diameter. Such a trend persists at higher temperature ($T = 255$ °C) when $d_{Pt} > 7.5$ nm. On the other hand, for Pt particles with $d_{Pt} < 7.5$ nm, the NO/H_2 reaction becomes more structure sensitive.

1. Introduction

The emission of greenhouse gas is partly related to the development of industrialized countries since 150 years [1]. More recently, the scientific community pointed out the relationship between anthropogenic emissions with climate changes. This led the European countries to sign the Kyoto Protocol [2] which committed themselves to reduce their emissions by at least 5% during the period 2008–2012 [3]. Particular attention was paid in the last two decades to anthropogenic N_2O emissions having a higher global warming potential ~300 times higher than that of CO_2 and a longer lifetime [3]. First attempts concerned adipic acid plants with outlet gas containing high concentration of N_2O (30–50 vol.%) as primary side product [4]. Significant reduction was successfully obtained using catalytic systems running at medium temperature in the absence of significant amount of water in the exhaust gas [5]. For nitric acid plants, the implementation of efficient N_2O abatement system is more challenging with the formation of significantly lower amount of N_2O from incomplete ammonia oxidation in the course of the deactivation of Pt–Rh gauzes used as catalyst for ammonia oxidation. A classification of different catalytic systems for N_2O abatement has been previously proposed according to their position in the process [6] as primary, secondary, and tertiary technologies. As illustrated in Fig. 1, primary solutions consist of modifying the oxidation process especially the design of the Pt–Rh gauzes to improve their thermal stability. Secondary technologies are commercially available

---

* Corresponding authors. Fax: +40 21 4100241 (V. Parvulescu), +33 3 20 43 65 61 (P. Granger).

E-mail addresses: vasile.parvulescu@g.unibuc.ro (V.I. Parvulescu), pascal.granger@univ-lille1.fr (P. Granger).

http://dx.doi.org/10.1016/j.jcat.2015.02.001

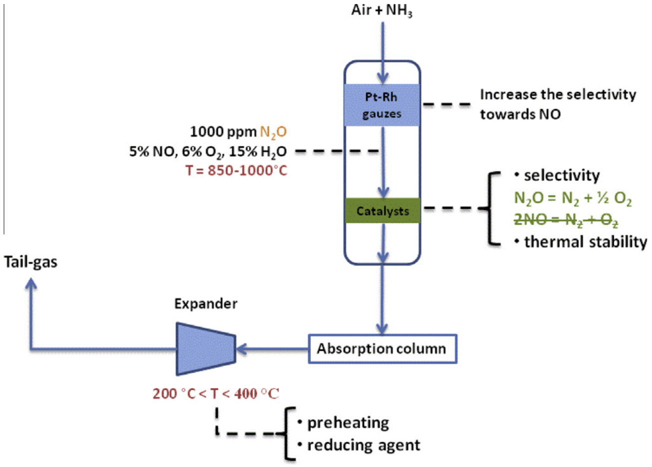

Fig. 1. Simplified scheme of an industrial plant for acid nitric production.

dedicated to the implementation of catalytic systems able to decompose N_2O at high temperature, for example, unsupported cobalt oxide spinel structures with composition $Co_{3-x}M_xO_4$ (M = Fe, Al, Co and $x = 0$–0.2) have been reported [7]. Yttrium-stabilized zirconia [8] and ceria–zirconia [9] were also investigated at the laboratory scale. According to this option, catalytic systems are installed inside the ammonia burner to convert N_2O immediately after its formation. Specific requirements are needed, especially a high thermal stability in wet atmosphere with running temperature above 900 °C and a good selectivity to avoid loss of nitric acid yield through partial NO conversion. Finally, tertiary technologies aim to convert N_2O and NO simultaneously either upstream or downstream the tail gas expander and need more intrinsically active phases such as precious metals. Generally, the use of reducing agents is requisite, especially for end-of-pipe technologies with low-temperature exhaust gas.

As a matter of fact, it has been already pointed out that the secondary technology is cost efficient, but its practicability is intimately related to the stability of the catalyst. It was earlier demonstrated that perovskite-type oxides can be profitably used for such an application. Previously, Porzellanwerk Kloster Veilsdor already patented supported $LaCoO_3$ perovskite as active phase for the decomposition of N_2O at high temperature [10]. Also, Umicore developed various compositions of perovskites [11]. The interest in the use of $LaCoO_3$ perovskite can be related to their peculiar properties developing specific surface after steam treatment at atmospheric pressure up to 800 °C as shown by Choudhary et al. [12]. However, at high temperature, significant surface reconstructions attributed to partial substitution of Co sites by Pd [13] or iron can occur [14] with the segregation of Co_3O_4. Incorporation of Rh has been previously envisaged for moderate- and high-temperature applications [15,16], especially for the decomposition of N_2O propellant [17,18]. High running temperature leads inevitably to losses of activity mainly due to sintering. To compensate deactivation effects, platinum group metals (PGM), especially Rh, which exhibits a much higher activity, can be added through conventional impregnation methods. However, the resulting material can also suffer from deactivation due to crystal transition and Rh volatilization [17]. Alternately, noble metals can be stabilized inside the perovskite structure or through reductive/oxidative pretreatments which can promote a greater stabilization of nano-sized noble metal particles [17]. The concept of intelligent catalysts was earlier associated with the self-regenerative behavior of noble metal-modified perovskites under three-way conditions with dynamic processes, which stabilize the metal dispersion contrarily to conventional catalysts supported on alumina where noble metals weakly interact and then irreversibly sinter [18–22]. Based on this concept, various strategies were developed to stabilize at the surface nanostructures such as those reported on Pt/CeO_2 [23] with the formation of nanocomposite oxides that involves the creation of a Pt–O–Ce bond. Similarly, strong interactions can be obtained when noble metals are conventionally deposited on perovskite via impregnation rather than sol–gel methods adopting optimal redox treatments to promote such type of interaction. Those transformations have been essentially characterized on $Pd/LaCoO_3$ and $Pd/LaFe_xCo_{1-x}O_3$ [24–26] corresponding to a possible stabilization of oxidic palladium species in unusual oxidation states and then exhibiting a high activity in NO_x conversion. A comparative investigation of Pt/Al_2O_3 and $Pt/LaFeO_3$ [27] also highlighted the same trend associated with the formation of Pt particles in strong interaction with $LaFeO_3$ providing a remarkable activity of $Pt/LaFeO_3$ compared to Pt/Al_2O_3 in the selective reduction of NO by H_2 at low temperature. Previous comparative investigations of the $NO/H_2/O_2$ reaction under lean conditions in wet atmosphere on Pt-based catalysts supported on conventional silica or alumina supports and on $La_{0.5}Ce_{0.5}MnO_3$ [28] or $La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$ [29] also report a significant rate enhancement when Pt interacts with perovskite supports. These authors also found a remarkable selectivity with rates of H_2 oxidation to H_2O on $La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$ of about 40% lower than that measured on Pt/SiO_2. Unfortunately, the simultaneous removal of N_2O is not possible at low temperature and requires reheating the exhaust gas to higher temperature [27]. Hence, based on these observations, the previous concept associated with the synthesis of smart catalysts involving reversible dynamic behaviors with noble metals going out and inside the perovskite structure during rich/lean oscillations can be revisited depending on the reducibility of the perovskite structure and the redox properties of PGM [25].

It will be shown in this present study that the stabilization of low amount of noble metals on mixed metal oxides is possible maintaining a high density of active sites at the surface through appropriate pre-activation thermal treatments. In such configuration, these optimized catalysts can be utilized for high-, moderate-, or low-temperature applications depending on the protocol used for PGM addition and the nature of the pre-activation thermal treatment. The abatement of N_2O from acid nitric plants offers an excellent example to combine these different approaches through the sequential catalytic abatement of N_2O (in the absence of reducing agent) during the first stage and then NO_x. Two different modes of noble metal incorporation will be investigated via sol–gel and wet impregnation depending on the running temperature of the catalytic application. It will be shown that appropriate redox thermal treatments lead to extensive surface reconstructions and to a densification of the active sites more stable under running conditions with enhanced catalytic properties. As a conclusion, a combined approach seems possible to reduce selectively N_2O at high temperature and efficiently NO at low temperature.

2. Experimental

2.1. Catalyst preparation

Stoichiometric perovskite-based catalysts ($LaCoO_3$ and $LaCo_{0.95}Pd_{0.05}O_3$) used for high-temperature applications were prepared according to a conventional sol–gel method via a citrate route [24]. Solid precursors obtained after drying overnight at 80 °C were calcined in air at 900 °C for 8 h. For end-of-pipe technology, $LaFeO_3$, prepared according to the same protocol, was calcined at 600 °C to maintain higher specific surface area. $LaFeO_3$ ($25\ m^2\ g^{-1}$) was impregnated by hexachloroplatinic acid solutions with adjusted concentration in order to obtain 1 wt.% Pt. The impregnated precursors were successively calcined in air at 400 °C and reduced at 300 °C or 500 °C in pure H_2.