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N_2O decomposition over doubly-promoted $Pt(K)/Al_2O_3–(CeO_2–La_2O_3)$ structured catalysts: On the combined effects of promotion and feed composition

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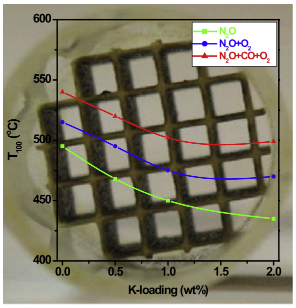
HIGHLIGHTS

- The de-N_2O efficiency of doubly-promoted $Pt(K)/Al_2O_3–(CeO_2–La_2O_3)$ catalysts is explored.
- Synergistic effect of structural ($CeO_2–La_2O_3$) and surface (K) promotion is revealed.
- The de-N_2O efficiency is enhanced in the order $N_2O + CO \gg N_2O > N_2O + O_2 > N_2O + O_2 + CO$.
- H_2O-induced inhibition on de-N_2O efficiency is largely reversible upon H_2O removal.
- The permanent portion of H_2O-induced deactivation is fully restored by H_2 treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study the feasibility of enhancing the N_2O decomposition activity of Pt supported on Al_2O_3, by means of combined structural and surface promotion is explored by employing: (i) support-mediated promotion by rare earth oxides (CeO_2, La_2O_3) incorporation into the Al_2O_3 support and (ii) surface-induced promotion by deposition of potassium. The study is conducted over structured catalysts suitable for practical applications, i.e., honeycomb cordierite monoliths washcoated with the catalyst composite. The chemical formula of the low active metal loaded (0.5 wt% Pt) doubly-promoted catalyst composite is: 0.5 wt%Pt(0–2 wt%K)/Al_2O_3–(16 wt%CeO_2 + 4 wt%La_2O_3). Assessment of the de-N_2O catalysts performance, either in the presence or absence of O_2, CO and H_2O in the feed steam, reveals the superiority of the doubly-promoted $Pt(K)/Al_2O_3–(CeO_2 + La_2O_3)$ catalysts in comparison to the bare Pt/Al_2O_3. Specifically, the de-N_2O performance of Pt/Al_2O_3 is dramatically enhanced by incorporation of 20 wt% $CeO_2–La_2O_3$ mixed oxide on the Al_2O_3 support and then further improved by 2 wt% K addition: the initial very poor de-N_2O efficiency of ca. 35% N_2O conversion at 600 °C over Pt/Al_2O_3 is led to 100% N_2O conversion at ca. 500 °C over the structural-promoted $Pt/Al_2O_3–(CeO_2 + La_2O_3)$, which is finally achieved at ca. 440 °C over the doubly-promoted Pt(2 wt%K)/$Al_2O_3–(CeO_2 + La_2O_3)$ monolith. In all cases (bare, structural- or doubly-promoted catalysts), the de-N_2O efficiency is strongly affected by the reaction conditions, following the sequence $N_2O + CO \gg N_2O > N_2O + O_2 > N_2O + O_2 + CO$. Water vapor and/or ($H_2 + O_2$) in the feed strongly suppresses the de-N_2O performance in a partially reversible manner. The de-N_2O efficiency, however, can be totally restored by H_2 addition into $N_2O + H_2O$ feed.

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1. Introduction

Nitrous oxide (N_2O) has been recently recognized as a powerful greenhouse gas with a Global Warming Potential (GWP) of about 300 times higher than that of CO_2. Furthermore, N_2O substantially contributes to the destruction of ozone layer, since it is photolyzed in the stratosphere, thus initiating a chain of cyclic reaction towards stratospheric ozone depletion [1–5].

Nowadays, the concentration of N_2O in the atmosphere has been increased by more than 10% compared to pre-industrial levels, mainly due to human activities. The latter primarily include the combustion processes (mobile and stationary), the use of fertilizers in land cultivation and the production of adipic and nitric acid [1–3]. Regarding combustion processes, it is clearly revealed by many studies that automotives, through Pt-group metals (PGMs)-based three-way catalytic converters (TWCs), are among the most significant sources of nitrous oxides: a significant portion of the NO during its reduction by CO or hydrocarbons in TWCs is converted to N_2O instead to N_2e.g. [6–8]. This justifies why the N_2O decomposition over Pt-group metals is of particular importance, at least, in three way catalytic chemistry e.g. [9,10].

With intensifying concern for environmental protection, several end-of-pipe technologies, such as thermal decomposition, plasma technology, selective adsorption and catalytic decomposition, have been employed for N_2O abatement from emission sources. Among them, the latter offers a number of advantages, including lower energy requirements and consequently lower cost [2–4].

A wide range of catalysts have been tested for N_2O decomposition, involving transition and noble metals supported catalysts, metal oxides, perovskites, mixed oxides and zeolites e.g. [2–4]. Among them, noble metal-based catalysts exhibit satisfactory activity even at low temperatures [3]. To this end, it has been demonstrated that Rh-based catalysts are among the most active for N_2O decomposition, with their reactivity however to be affected by the reaction conditions. In accordance to Centi et al. [10], the formation of Rh_2O_3 under oxidizing conditions notably prohibits the de-N_2O process. Recent studies, however, clearly revealed that $Rh^{\delta+}$ species are more active than Rh^0 for N_2O decomposition over Rh supported on La- or Pr-doped CeO_2 [11]. In accordance to the authors, the stabilization of $Rh^{\delta+}$ species through metal oxide-support interactions plays a key role in the activity of these catalysts. In a similar manner, DFT calculations in conjunction with *ab initio* thermodynamics and density of state analysis clearly reveal that Rh_2O_3 surfaces exhibit high Lewis acidity, resulted from electron acceptor sites [12]. According to the authors the latter could explain the high reactivity towards N_2O dissociation over Rh_2O_3.

On the other hand, the de-N_2O performance of Pt-based catalysts is notably hindered by strongly adsorbed oxygen atoms, originating either from gas phase or N_2O decomposition [13,14]. The existence of reducing agents can facilitate scavenging of surface oxygen species; that is why hydrocarbons co-feed has been often considered as an alternative approach in Pt-catalyzed de-N_2O processes [15]. Moreover, since N_2O adsorption is generally considered to proceed *via* a charge donation from metals sites to N_2O unoccupied molecular orbitals, the electronic state of active sites is expected to play a crucial role in N_2O bonding and subsequent scission [16]. Towards this direction, considerable efforts have been recently devoted on modifying the intrinsic characteristics of active sites *via* the use of structural [17–19] or surface modifiers [20–25].

Considering the use of structural modifiers, cerium oxide has been extensively studied as support [26,27] or support dopant [17–19] in de-N_2O process. Due to its unique redox properties ceria can affect the reducibility of active sites and consequently the de-N_2O performance. In this context, it was recently found that the nature of support (Al_2O_3 or CeO_2) substantially affects the activity of noble metals (Pt, Pd, Rh) [26,27]; in almost all cases CeO_2–based catalysts demonstrate superior activity, ascribed mainly to noble metal/ceria interactions. In a similar manner, Granger and Leclercq [18] found that incorporation of CeO_2 in Al_2O_3 support in bimetallic Pt-Rh/Al_2O_3 results to an enhancement in de-N_2O performance. According to the authors, the beneficial effect of ceria could be associated with the participation of metal-support interfacial sites in N_2O decomposition.

In a recent communication [19], dealing with the impact of lanthanide oxides as support additives on N_2O decomposition, we have shown that the de-N_2O efficiency of Pt/Al_2O_3 washcoated monoliths can be greatly enhanced by incorporation of CeO_2–La_2O_3 mixed oxides into Al_2O_3 support; complete conversion of N_2O was attained over Pt/Al_2O_3–(CeO_2–La_2O_3) catalysts at ca. 500 °C and a Gas Hourly Space Velocity (GHSV) of 10,000 h^{-1} even in the presence of excess O_2, in opposite to the unmodified Pt/Al_2O_3 catalyst, which offered N_2O conversion less than ~20% at 600 °C [19]. Based on *in situ* diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) measurements, the superior catalytic performance of modified samples was attributed to the formation of electron enriched Pt sites ($Pt^{\delta-}$), located at metal-support interfacial area, which are highly active towards N_2O decomposition.

However, besides structural modifiers, electropositive promoters, such as alkalis or alkaline earths, have also been reported to play a key role on de-N_2O process over several catalytic systems e.g. [20–23]. In particular, it was been found that addition of Cs on NiO [20] or CuO [21] and Li, Na, K, Cs or Sr on Rh/Al_2O_3 [22,23] results to a considerable increase in N_2O decomposition efficiency of these catalysts. In agreement with the above, we have recently shown that the surface and catalytic properties of Pd/Al_2O_3 catalysts during the N_2O decomposition in the presence of hydrocarbons can be substantially altered by potassium (K), which was supplied either electrochemically [24] or conventionally [25] onto the catalyst surface. In particular, it was found that potassium strongly enhances the N_2O decomposition rate, resulting in notably lower N_2O *light-off* temperatures (of about 100 °C) compared to the un-promoted catalyst. Based on a surface characterization study [25], involving XPS, *in situ* DRIFT spectroscopy of CO adsorption and FTIR-pyridine adsorption, it was revealed that the electronic properties of Pd/Al_2O_3 catalyst can be substantially modified by potassium addition, which in turn affects the reactants' chemisorptive bonds and consequently the de-N_2O activity.

Motivated by the pronounced impact of structural and surface modifiers, recently we have developed highly effective and thermally stable Rh-free (Pt-only) three way converters (TWCs), in an effort to avoid the use of rare Rh in TWCs [28,29]. This was accomplished through a synergistic structural and surface promotion by modifying the TWC washcoat with 20 wt% of $Ce_{0.8}La_{0.2}O_{1.9}$ (structural promoter) and sodium (surface promoter): Pt(Na)/Al_2O_3–(CeO_2 + La_2O_3) [29]. It is therefore obvious, that the de-N_2O behavior of these economic and highly effective materials is of considerable interest, explaining our motivation for materials selection in the present investigation.

Finally, taking into account that the majority of N_2O decomposition studies have been performed with catalysts in the form of powders (i.e., incompatible for direct practical use) it is of particular interest to investigate the de-N_2O process in practical configurations (i.e., in the form of washcoated cordierite monoliths), that offer several practical advantages, including scale-up aspects [3].

Based on the above, the present study aims to investigate possible synergistic effects of structural and surface modifiers towards N_2O decomposition. To this end, doubly-promoted catalysts, i.e. Pt(K)/Al_2O_3–(CeO_2–La_2O_3), were prepared by incorporation of rare earth oxides into Al_2O_3 carrier and subsequent modification of the active phase by potassium. For practical purposes, the as prepared