Study by isotopic gases and *in situ* spectroscopies (DRIFTS, XPS and Raman) of the N_2O decomposition mechanism on Rh/CeO$_2$ and Rh/γ-Al$_2$O$_3$ catalysts

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ABSTRACT

The N$_2$O decomposition mechanism on Rh/CeO$_2$ and Rh/γ-Al$_2$O$_3$ catalysts has been studied by pulses of isotopic N$_2$O and O$_2$ together with *in situ* DRIFT, XP and Raman spectroscopies. The higher catalytic activity of Rh/CeO$_2$ in comparison with Rh/γ-Al$_2$O$_3$ is related to the Rh–CeO$_2$ interaction and to the participation of the CeO$_2$ support in the N$_2$O decomposition mechanism, γ-Al$_2$O$_3$ being an inert carrier. Rhodium on Rh/γ-Al$_2$O$_3$ is reduced to Rh^0 under reaction conditions and N$_2$O decomposition over this catalyst mainly occurs via the Eley–Rideal mechanism. On the contrary, the ceria support interacts strongly with rhodium partially stabilizing cationic species of the noble metal during N$_2$O decomposition. In Rh/CeO$_2$, the reduced rhodium sites (by N$_2$O) can be reoxidized afterwards either by N$_2$O or by ceria oxygen, and the vacant sites created on the ceria support are then oxidized by N$_2$O. The active sites for N$_2$O chemisorption and decomposition are not only located on rhodium but also on ceria.

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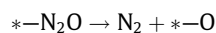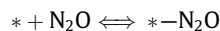
1. Introduction

The environmental impact of N$_2$O has attracted strong attention because of its contribution to global warming and ozone depletion in the upper atmosphere [1]. N$_2$O is emitted as a by-product in several chemical processes of high industrial relevance, such as nitric acid and adipic acid production. In addition, N$_2$O emission by vehicles also takes place due to the ageing of the catalytic converters used for NO$_x$ emissions abatement.

The most effective solution to remove N$_2$O from gas streams is to use catalysts to either promote N$_2$O decomposition or to facilitate its reaction with a reducing agent. The former process is preferred because additional reactants are not required, and several catalysts have been developed for N$_2$O decomposition [1].

Several mechanisms have been proposed to describe the catalytic decomposition of N$_2$O [1–6]. The study of these mechanisms is based, in most cases, on the analysis of the effect of the N$_2$O partial pressure and temperature on the N$_2$O decomposition rate. The catalytic N$_2$O decomposition reaction has been described as a molecular adsorption of N$_2$O on active sites of the catalyst (∗) followed by the decomposition of the N$_2$O molecule with N$_2$ release.

$$\ast + N_2O \Longleftrightarrow \ast{-}N_2O$$

$$\ast{-}N_2O \rightarrow N_2 + \ast{-}O$$

Transient kinetic studies performed with MnO$_2$, for instance, demonstrated that not all the adsorption sites suitable for N$_2$O adsorption are active for N$_2$O decomposition [7]. On the other hand, depending on the catalyst nature, dissociative chemisorption of N$_2$O can occur in a single step instead of molecular adsorption followed by surface decomposition:

$$\ast + N_2O \rightarrow N_2 + \ast{-}O$$
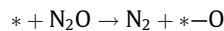
The oxygen atoms left on the active sites (∗–O) can be desorbed by recombination, with O$_2$ release (Langmuir–Hinshelwood mechanism):

$$2\ast{-}O \Longleftrightarrow 2\ast + O_2$$

or by reaction with another N$_2$O molecule (Eley–Rideal mechanism):

$$\ast{-}O + N_2O \rightarrow \ast + N_2 + O_2$$
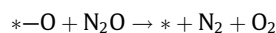
Note that the recombination of oxygen atoms is a reversible process, while the regeneration of active sites by N$_2$O is irreversible [4]. The reversibility of the former reaction explains why O$_2$ has an inhibitory effect on most N$_2$O decomposition catalysts, since N$_2$O and O$_2$ compete for the active sites of the catalyst [4].

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The interaction of the O_2 molecules with catalytic surfaces has been deeply studied [8–13], and the knowledge about these interactions is useful to explain some aspects of the N_2O decomposition mechanism and to develop catalysts for N_2O decomposition in O_2-rich streams. Isotopic gases are very useful to study the interaction of gas molecules with solid catalysts, and many studies have been carried out with $^{18}O_2$ [14,15]. From these studies, it has been concluded that there are three main processes involved in the oxygen exchange mechanisms between molecular oxygen and metal oxide surfaces: the dissociative chemisorption of molecular oxygen, the exchange of atoms or adsorbed ions and desorption of molecular oxygen. The exchange of oxygen atoms can occur in a single step or in two consecutive steps, and the nature of the solid surface significantly affects these processes.

Among the different catalysts studied for N_2O decomposition, Rh catalysts are highly active, and the activity depends on the support used [16,17]. Ceria-based supports, either pure or doped with La or Pr, for instance, enhance the catalytic activity of rhodium with regard to alumina supports. This improvement seems to be related to the redox properties of ceria, and it was suggested that cerium oxide is also involved in N_2O decomposition. However, the reaction mechanism behind such enhanced performance of rhodium when supported on ceria is still unknown.

The interaction of ceria-based oxides with isotopic O_2 has been widely studied [9,18–20], and the oxygen exchange capacity of this type of oxides is extremely high and fast. In some cases, the interaction of ceria-based materials with some other oxygen-containing isotopic gases different to $^{18}O_2$ has been studied. For example, Cunningham et al. [18] studied the exchange of oxygen between $^{15}N^{18}O$ and CeO_2, which takes place from 175 °C, and evidences of the oxygen exchange between $C^{18}O_2$ and CeO_2 have also been reported [21,22]. The oxygen exchange mechanism between isotopic CO_2 and Pt/CeO_2 catalyst occurs in two consecutive steps, and the exchange of both $C^{18}O_2$ oxygen atoms prevails with regard to the single exchange. However, as far as we know, the interaction of isotopic N_2O with Rh/ceria catalysts has not been reported.

The aim of this study is to determine the rhodium-catalysed N_2O decomposition mechanisms, in order to understand the improved activity of Rh/ceria with regard to Rh/alumina catalysts. The approach followed combines pulse experiments of isotopic N_2O and isotopic O_2 with in situ XPS, DRIFTS and Raman spectroscopy experiments. The combination of all these techniques provides complementary information about the reaction mechanisms. The experiments with isotopic gases provide information about the participation of catalyst oxygen in the N_2O decomposition mechanism, in situ DRIFTS allows monitoring the surface nitrogen groups during the reaction and in situ XPS and in situ Raman spectroscopy are useful to identify changes in the catalyst during N_2O decomposition, such as changes in the oxidation states of the metals involved in the reaction mechanism.

2. Experimental

2.1. Catalysts preparation

Two powder catalysts have been used in this study, which are referred to as Rh/CeO_2 and Rh/γ-Al_2O_3. The CeO_2 support was prepared by $Ce(NO_3)_3 \cdot 6H_2O$ (Aldrich, 99.9%) calcination in static air at 600 °C for 90 min (heating rate 10 °C/min). The γ-Al_2O_3 support was prepared from commercial γ-Al_2O_3 pellets (Across), which were crushed in a mortar. Rh was loaded on the CeO_2 and γ-Al_2O_3 supports (125–200 μm particle size) by incipient wetness impregnation with a water solution of $Rh(NO_3)_3$ (Sigma Aldrich, 99.9%). Finally, both catalysts were dried at 200 °C and calcined at 500 °C for 2 h. The target content of Rh in both catalysts, after calcination, was 0.5 wt.%.

The supports and catalysts were characterized by Raman spectroscopy, XRD, N_2 adsorption at −196 °C, H_2–TPR and TEM, and detailed information about such characterization was reported elsewhere [16]. Briefly, it is important to mention that both supports present similar BET surface area (76 m^2/g CeO_2 and 78 m^2/g γ-Al_2O_3) and similar rhodium particle size (average size of rhodium particles 2.2 nm in Rh/CeO_2 and 2.3 nm in Rh/γ-Al_2O_3, as observed by TEM).

2.2. N_2O decomposition tests in a fixed-bed reactor

N_2O decomposition tests were performed at atmospheric pressure in a 10-mm i.d. cylindrical fixed-bed reactor, with 100 mg of catalyst diluted with 700 mg of SiC and a total gas flow of 100 ml/min (GHSV = 10,000 h^{-1}). The catalytic bed was packed between plugs of quartz wool. Different N_2O/He mixtures, with N_2O concentrations of 100, 300, 600, 1000 and 1400 ppm were evaluated, and experiments with 1000 ppm $N_2O/5\%$ O_2/He were also performed. The gas composition was analysed by a HP 6890 gas chromatograph equipped with a thermal conductivity detector and two serial columns (Porapak Q, for N_2O, and Molecular Sieve 13X, for O_2 and N_2).

The experiments consisted of point-by-point isothermal reactions in the range 200–400 °C, and all reactions were extended to the steady state (typically between 20 and 40 min were needed). A typical experiment consisted of heating the as prepared (fresh) catalyst under the selected gas flow at 200 °C, where N_2O decomposition does not occur in any case. Once all gas concentrations are stable, the temperature is raised 25 °C, and this procedure is repeated to 400 °C. Then, the temperature is lowered to room conditions under He flow, the next gas mixture to be studied is fed to the reactor and the heating steps are repeated as described. All experiments have been carried out with the same sample of each catalyst. In order to ensure that their catalytic activity does not change during the catalytic cycles, catalytic tests under 1000 ppm N_2O/He have been performed as control tests every few catalytic cycles. As will be discussed afterwards, only the Rh/γ-Al_2O_3 catalyst showed different catalytic activity during the first and second runs performed (under identical conditions), but not in further cycles where the catalytic activity of the second cycled is maintained.

2.3. XPS characterization after in situ treatments under reaction conditions

XPS experiments were carried out in a VG-Microtech Multilab electron spectrometer using Mg Kα (1253.6 eV) radiation source. To obtain the XPS spectra, the pressure of the analysis chamber was maintained at 5×10^{-10} mbar. The binding energy (BE) and the kinetic energy (KE) scales were adjusted by setting the C1s transition at 284.6 eV, and BE and KE values were determined with the software Peak-fit of the spectrometer. XPS spectra of the fresh catalysts Rh/CeO_2 and Rh/γ-Al_2O_3 and after 1 h in situ treatments under 1000 ppm N_2O/Ar or pure Ar at different temperatures between 250 and 325 °C were recorded. The in situ treatments were carried out before the XPS measurement in an auxiliary reaction chamber, where the sample is heated to the selected temperature, and the gas mixture is fed at 1 atm total pressure. After the treatment, the sample was introduced into the XPS chamber avoiding exposure to air, and spectra were recorded at room temperature.

2.4. In situ Raman spectroscopy experiments

Raman spectra were recorded in a multichannel dispersive Raman spectrometer (Labram from Jobin–Yvon Horiba) with a laser source He:Ne (632.8 nm) using a Peltier cooled CCD as a detector.