Catalytic conversion of N_2O to N_2 over metal-based catalysts in the presence of hydrocarbons and oxygen

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The catalytic conversion of N_2O to N_2 in the presence or the absence of propene and oxygen was studied. The catalysts examined in this work were synthesized impregnating metals (Rh, Ru, Pd, Co, Cu, Fe, In) on different supports (Al_2O_3, SiO_2, TiO_2, ZrO_2 and calcined hydrotalcite $MgAl_2(OH)_8 \cdot H_2O$). The experimental results varied both with the type of the active site and with the type of the support. Rh and Ru impregnated on γ-alumina exhibited the highest activity. The performance of the above most promising catalysts was studied using various hydrocarbons (CH_4, C_3H_6, C_3H_8) as reducing agents. These experimental results showed that the type of reducing agent does not affect the reaction yield. The temperature where complete conversion of N_2O to N_2 was measured was independent of the reductant type. The activity of the most active catalysts was also measured in the presence of SO_2 and H_2O in the feed. A shift of the N_2O conversion *versus* temperature curve to higher temperatures was observed when SO_2 and H_2O were added, separately or simultaneously, to the feed. The inhibition caused by SO_2 was attributed to the formation of sulfates and that caused by water to the competitive chemisorption of H_2O and N_2O on the same active sites.

KEY WORDS: N_2O; nitrous oxide; reduction; decomposition; Rh; Ru; SO_2; H_2O.

1. Introduction

N_2O emitted from anthropogenic sources contributes to the greenhouse effect and to the destruction of the ozone layer. N_2O is present in relatively low concentrations in the troposphere (about 310 ppb); however, it is included in the powerful greenhouse gases. N_2O is very stable in air and its atmospheric lifetime is *ca.* 150 years. The atmospheric concentration of N_2O increases at a rate of about 0.37% per year. The only way to decrease the N_2O emissions is to limit the emissions derived from anthropogenic activities. Chemical processes associated with the production and use of nitric acid and fluidized bed combustion are two of the main nitrous oxide sources, since their contribution to the total N_2O emissions is about 20% [1]. The public awareness and sensitivity on environmental issues motivated the European Union to commit itself to reduce the greenhouse gases by 5–8% by 2012. This implies that the development of an efficient technology for control of N_2O emissions is a priority.

The catalytic decomposition and the selective catalytic reduction (SCR) of N_2O to N_2 are two candidate technologies, which can he applied to reduce the emissions of this harmful gas. The selective catalytic reduction of N_2O was studied only over Cu/ZSM-5 and Fe/ZSM-5 catalysts [2–5]. Both catalysts exhibited high activity under ideal reaction conditions (absence of poison gases). Fe/ZSM-5 maintained most of its initial activity after the addition of H_2O to the feed, while the H_2O presence caused a shift of the N_2O conversion *versus* temperature curve to higher temperatures over Cu/ZSM-5. Centi and Vazzana [3] examined the tolerance and the durability of Fe/ZSM-5 for the N_2O reduction using a feed that simulated flue gases (presence of O_2, H_2O and SO_2). About 60% of the N_2O was reduced to N_2 for more than 600 h in the presence of 500 ppm SO_2. SO_2 was not oxidized to SO_3 over the catalyst and this caused the tolerance of this catalyst to the SO_2 presence, according to the above authors.

The N_2O reduction by CO [6] or CH_4 [7] was examined in the absence of O_2. NH_3 has also been used as a reducing agent [8,9] resulting in high N_2O conversions over Ru and Rh zeolitic catalysts. However, the presence of 3% O_2 caused a significant inhibition of the reaction.

Catalytic decomposition has been studied more than the SCR of N_2O over different catalytic systems [3,10–18]. Parameters that affect the decomposition rate over an active site are the type of the support and the presence of other gases (O_2, H_2O, SO_2). Most of the catalysts under realistic reaction conditions exhibited low activity [1]. The presence of O_2 and other gases such as SO_2 and H_2O that typically exist in flue gas streams inhibited the catalysts' activity [14,17,19,20]. Rh supported on TiO_2 and on ZSM-5 lost most of its activity when O_2, H_2O or SO_2 was added to the feed according to Centi *et al.* [14]. Lower N_2O decomposition rates were measured

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by Chang *et al.* [15] in the presence of excess oxygen over Ru/ZSM-5. The above authors postulated that at low temperatures O_2 desorption is the rate-limiting step; therefore, high O_2 concentrations suppress the extent of the reaction.

The effect of the type of the support and the Rh dispersion on the N_2O decomposition was studied by Yazaki *et al.* [21]. Rh supported on USZ and alumina was more active than that supported on FSM-16, CeO_2, ZrO_2 and La_2O_3. The mechanism of O_2 desorption during the N_2O decomposition over Rh/USZ was the Langmuir–Hinshelwood, and reaction-assisted desorption of O_2 occurred at low temperatures [22,23].

N_2O decomposition is inhibited by SO_2 because SO_2 is oxidized to SO_3 and it subsequently forms sulfates [14,17]. However, Perez-Ramirez *et al.* [24] reported that the presence of Mg in Ni-HTLc and Co-HTLc catalysts prevents the deactivation of the catalysts due to the preferential adsorption of SO_2/SO_3 on the MgO phase. In this way, the active sites are free for the N_2O reduction. The N_2O decomposition rate is higher in a dry stream than that in a wet one [10–13,18,19]. The loss of activity due to the H_2O presence is reversible. This behavior was attributed to the competitive adsorption of H_2O and N_2O on the catalytic surface. On the other hand, Zeng and Pang [13] postulated that the deactivation of Ru/Al_2O_3 by H_2O is the result of chemical constituent changes (acidity–basicity of the catalyst).

Previous experimental works have shown that the presence of oxygen that typically exists in flue gases derived from fluidized bed combustors inhibits the activity of most catalysts. The commercial application of N_2O reduction catalysts requires catalytic activities not only in the presence of oxygen, but also in the presence of other poison gases such as H_2O and SO_2. The purpose of this work is to present the performance of a series of metal-based catalysts efficient for the N_2O reduction. Catalysts based on different metal active sites and supported on different metal oxide carriers were tested. We chose to add traces of propene and excess O_2 in the feed of most experiments of this study because the former gas is typically employed in SCR studies and the latter one is present in most flue gases. Finally, the resistance of the most promising catalysts to the presence of poison gases (H_2O, SO_2) was examined.

2. Experimental

2.1. Materials

A series of Rh-, Ru-, Pd-, In-, Fe-, Cu-, and Co-based on alumina catalysts were prepared using the dry impregnation technique. γ-alumina was supplied by Engelhard in extrudates which were crushed and sieved to separate the particles of 180–355 μm. In order to examine the effect of the type of the support on the catalyst performance we deposited Rh on various supports, namely SiO_2 (Grace), TiO_2 (Norton), ZrO_2 (Norton) and hydrotalcite $MgAl_2(OH)_8 \cdot H_2O$ (Condea). The MgO/Al_2O_3 ratio was equal to 7/3 in the last sample. Before the impregnation, hydrotalcite was calcined at 650 °C for 2 h in order to remove the water content. All supports were in the same particle size with γ-alumina. Water solutions of the corresponding metal salts were impregnated on the carriers. Following the impregnation, the catalysts were dried at 120 °C for 2 h and then they were calcined at 600 °C or 500 °C, under air flow. The metal content in each of the catalysts was measured by the ICP/AES technique. A list of catalysts is given in table 1 along with the calcination conditions, the percentage of the active sites and the precursor salt.

2.2. Experimental setup

Reactivity experiments were carried out in a laboratory-scale reaction unit. The unit consists of the feed gas

Table 1
List of prepared catalysts

Catalyst	Calcination conditions	Metal loading	Metal salt
Rh/Al_2O_3	600 °C/9 h with air	2% Rh	$RhCl_3$
Rh/ZrO_2	600 °C/9 h with air	2% Rh	$RhCl_3$
Rh/TiO_2	600 °C/9 h with air	2% Rh	$RhCl_3$
Rh/SiO_2	600 °C/9 h with air	2% Rh	$RhCl_3$
Rh/HTlc7	600 °C/9 h with air	1.6% Rh	$RhCl_3$
Ru/Al_2O_3	550 °C/6 h with air	2% Ru	$RuCl_3$
Pd/Al_2O_3	500 °C/6 h with air	2% Pd	$PdCl_3$
Fe/Al_2O_3	500 °C/6 h with air	2% Fe	$Fe(NO_3)_3$
Co/Al_2O_3	500 °C/6 h with air	1% Co	$Co(NO_3)_2$
In/Al_2O_3	600 °C/6 h with air	2% In	$In(NO_3)_3$
Cu/Al_2O_3	500 °C/6 h with air	2% Cu	$Cu(NO_3)_2$

system, a fixed-bed reactor and the gas analysis system. Gases of standard composition were initially mixed and then introduced into a quartz reactor of 1.7 cm i.d. The composition of the reactive gas during the N_2O reduction experiments was 500 ppm N_2O, 1000 ppm hydrocarbon, 5% O_2, 0 or 50 ppm SO_2, 0 or 10% H_2O in He. Propene, propane or methane was used as reductant. When water was added to the reactive gas mixture, pure He was saturated with water at 50 °C and the H_2O/He gas mixture was mixed with the other gases. In this case, all lines prior to the reactor were heated at 100 °C to avoid any water condensation. The reactor loading was 1 g and the flow rate was 500 cc/mm. As a result, the catalyst to flow ratio (W/F) was 0.12 g s cm^3. More details about the reaction unit can be found elsewhere [25].

The composition of the exit gas stream was analyzed by a series of analyzers and a gas chromatograph (GC). The concentration of the following gases was measured by the analyzers: N_2O (NDIR, VIA-510 Horiba), NO_x (Chemiluminesence, Thermo Environmental 42C-HL), CO_2 (NDIR, VIA-510 Horiba), CO (NDIR, VIA-510 Horiba), O_2 (paramagnetic, MPA-510 Horiba) and SO_2 (NDUV, AR 3000 Anarad). Gas samples were automatically injected in a HP GC equipped with TCD and FID detectors. The former detector was used for the N_2 and the latter one for hydrocarbon concentration measurements.

3. Results and discussion

3.1. Effect of active site on the N_2O reduction (presence of C_3H_6 and O_2)

Pure γ-alumina and alumina-based catalysts were initially tested as catalysts for the N_2O reduction in the presence of C_3H_6 and O_2. The experimental data of figure 1 show that unpromoted alumina exhibits very low activity for the reduction of N_2O to N_2. The deposition of an active metal on alumina enhanced the activity. Complete conversion of N_2O to N_2 was observed over Rh/Al_2O_3 and Ru/Al_2O_3 at 480 °C. The other alumina-based catalysts exhibited significantly lower activity at temperatures lower than 600 °C. Among these catalysts Fe/Al_2O_3 was the most active and Co/Al_2O_3 the least active. The activity of the catalysts shown in figure 1 follows the order $Rh \geq Ru > Fe > Pd > In > Co$. The shape of the N_2O conversion *versus* temperature curves (solid lines) is different from the typical NO_x conversion *versus* temperature curve [26–28]. At low temperatures both curves follow a sigmoidal pattern; however, at higher temperatures the N_2O conversion reaches 100% and remains stable, while the NO_x conversion drops. On the other hand, the shape of the propene conversion *versus* temperature curves (dashed lines) is sigmoidal both in the NO_x and N_2O reduction experiments. Propene is consumed very fast over Pd/Al_2O_3, a

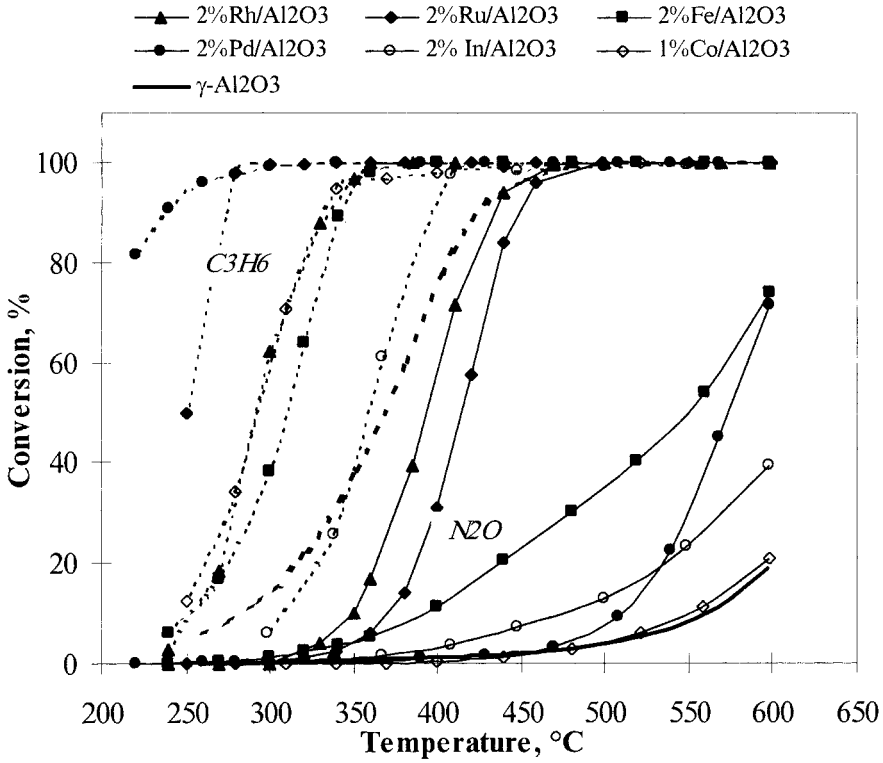


Figure 1. Conversion of N_2O (solid lines) and C_3H_6 (dashed lines) over alumina and alumina-based catalysts. Feed: 500 ppm N_2O, 1000 ppm C_3H_6, 5% O_2, balance He.

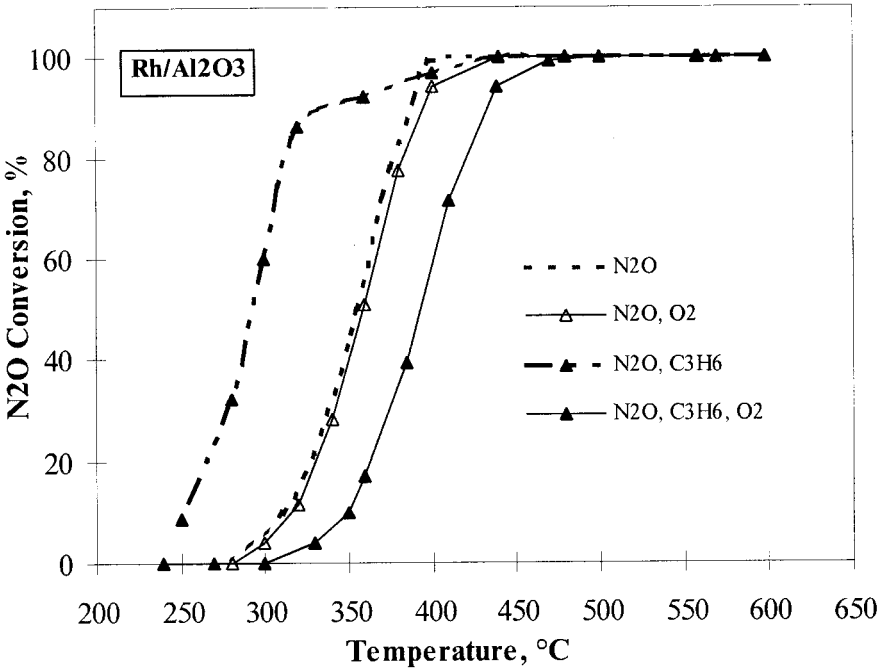


Figure 2. Conversion of N_2O to N_2 over Rh/Al_2O_3 catalyst, in the presence and in the absence of O_2 and C_3H_6. Feed: 500 ppm N_2O, 0 or 1000 ppm C_3H_6, 0 or 5% O_2, balance He.

well-known oxidizing catalyst, followed by Ru/Al_2O_3. The propene conversion curves over Rh/Al_2O_3, Co/Al_2O_3 and Fe/Al_2O_3 almost coincide, while propene is burned over In/Al_2O_3 and pure Al_2O_3 at higher temperatures. However, over all samples of figure 1 propene reaches complete conversion at temperatures significantly lower than those of complete N_2O reduction. As a result, at temperatures higher than that of complete propene consumption, the reductant is present only in a part of the catalytic bed. When the temperature of reaction rises the portion of the catalytic bed that sees propene decreases. Given that under these conditions complete reduction of N_2O is observed, we postulate that in the main N_2O is catalytically decomposed to N_2.

3.2. Role of O_2 and reductant on the N_2O reduction

We performed a series of experiments aiming at the elucidation of the O_2 and C_3H_6 role during the N_2O reduction. We chose the two most active catalysts of figure 1, namely Rh/Al_2O_3 and Ru/Al_2O_3, for these experiments and we varied the feed composition. The dashed line in figure 2 shows the conversion of N_2O to N_2 in the absence of both O_2 and C_3H_6 over Rh/Al_2O_3. The light-off temperature is 300 °C and at 400 °C more than 90% of N_2O is reduced. Other researchers, as well, observed similar experimental data for the catalytic decomposition of N_2O to N_2. Specifically, Yuzaki *et al.* [29] and Schulz *et al.* [17] measured complete decomposition of N_2O to N_2 at 400 °C over Rh/Al_2O_3. The same conversion of N_2O to N_2 was also measured over zeolites and hydrotalcites [10,30].

Addition of O_2 in the feed (figure 2) had no influence on the decomposition of N_2O to N_2. This implies that oxygen is not adsorbed on the catalyst competitively with N_2O. Moreover, the presence of 5% O_2 does not inhibit the desorption of O_2 derived from the N_2O reduction. Satsuma *et al.* [7] studied the N_2O decomposition over various metal oxide catalysts in the presence and in the absence of O_2. They classified the metal oxides according to the O_2 effect on the N_2O reduction into two categories: those that were not affected and those that were inhibited by the oxygen presence in the feed. Alumina was among the materials of the former category.

We replaced O_2 with C_3H_6 in the feed (absence of O_2) and we observed a significant enhancement of the N_2O conversion to N_2 expressed as a shift of the N_2O conversion *versus* temperature curve to lower temperatures. The catalytic reduction of N_2O by propene proceeds via the reaction

$$9N_2O + C_3H_6 \rightarrow 9N_2 + 3CO_2 + 3H_2O. \quad (1)$$

The catalytic decomposition of N_2O follows the decomposition mechanism (1) described by the reactions

$$N_2O + * \leftrightarrow N_2O* \quad (2)$$

$$N_2O* \leftrightarrow N_2 + O* \quad (3)$$

$$2O* \leftrightarrow O_2 + 2* \quad (4)$$

$$N_2O + O* \rightarrow N_2 + O_2 + * \quad (5)$$

where $*$ is an active site.

In the absence of O_2 in the bulk phase, propene is used to remove the surface oxygen formed from the N_2O

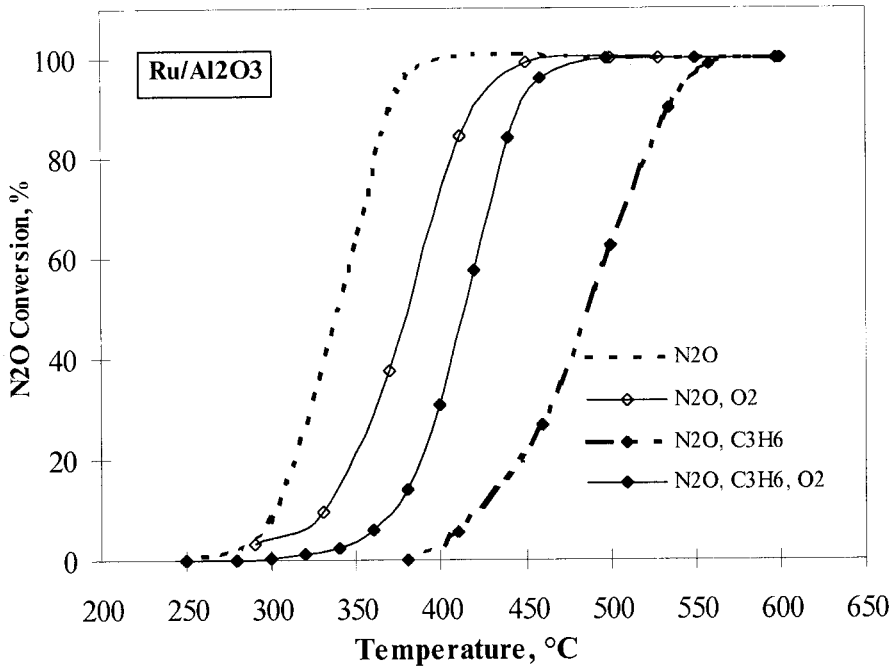


Figure 3. Conversion of N_2O to N_2 over Ru/Al_2O_3 catalyst, in the presence and in the absence of O_2 and C_3H_6. Feed: 500 ppm N_2O, 0 or 1000 ppm C_3H_6, 0 or 5% O_2, balance He.

decomposition according to the reactions

$$C_3H_6 + 9O* \rightarrow 3CO_2 + 3H_2O + 9* \quad (6)$$

$$C_3H_6* + 9O* \rightarrow 3CO_2 + 3H_2O + 10*. \quad (7)$$

The "cleanup" of the catalytic surface by propene (in the bulk phase or adsorbed) favors the dissociative adsorption of N_2O. Moreover, propene can modify the oxidation stage of the Rh active sites leading to partially reduced sites. During the selective catalytic reduction of NO_x with propene over Rh/Al_2O_3, partial reduction of Rh_2O_3 was observed in our previous work [31]. This was verified by XPS measurements performed in this work, where we observed partial reduction of Rh as a result of the N_2O presence. This reduction was more pronounced in the absence of O_2. Therefore, the presence of propene in the feed may benefit the N_2O reduction to N_2, both consuming oxygen derived from N_2O and reducing the active sites.

When oxygen was added to the feed (feed: N_2O, C_3H_6 and O_2), the N_2O *versus* temperature curve was shifted toward higher temperatures by about 80 °C as compared with experiments where N_2O/He or N_2O/C_3H_6/He were fed (figure 2). When both bulk O_2 and N_2O coexist in the feed, propene adsorbed on the active sites is selectively oxidized by O_2, thus inhibiting the N_2O reduction. In the absence of O_2, N_2O is catalytically decomposed to N_2 and catalytically reduced by C_3H_6. However, in the presence of O_2 the latter mechanism of N_2 formation is inhibited and N_2O competes with C_3H_6 for the same sites.

In figure 3 we present experimental results for different feeds over Ru/Al_2O_3. The N_2O conversion curves over Ru/Al_2O_3 and Rh/Al_2O_3 were similar when the feed contained N_2O only. However, addition of O_2 in the feed caused a shift of the N_2O decomposition curve to higher temperatures (*ca.* 60 °C) over the former sample and had no effect over the latter one. Given that both fresh samples are fully oxidized, the presence of O_2 in the feed is not expected to modify their oxidation state. As a result, we attribute the difference in the N_2O conversion curves between the two alumina-based samples to the adsorption characteristics on the metal active sites. We believe that O_2 is adsorbed on Ru more strongly than on Rh, thus inhibiting the N_2O reduction in the former sample. In accordance to these results, Zeng *et al.* [13] noticed that the inhibition caused by O_2 depended on the temperature.

Another interesting difference between the performance of Ru/Al_2O_3 and Rh/Al_2O_3 is the significant inhibition of the N_2O reduction by C_3H_6 over the former sample (figure 3), while the inverse was observed over the latter one (figure 2). Specifically, complete conversion of N_2O was measured above 560 °C in the presence of N_2O and C_3H_6, while in the absence of C_3H_6 this temperature was 400 °C over Ru/Al_2O_3. XRD and XPS measurements of this work agree with previous measurements [13] that fresh Ru supported on alumina is in the form of RuO_2 (oxidation state +4). Furthermore, our XPS measurements showed that when N_2O and C_3H_6 exist in the feed, Ru is reduced to its metallic form, while addition of O_2 inhibits the reduction of ruthenium oxides. Chang and coworkers [15,16] support that RuO_2 and its related oxides RuO_x are good electron conductors with high chemical stability.

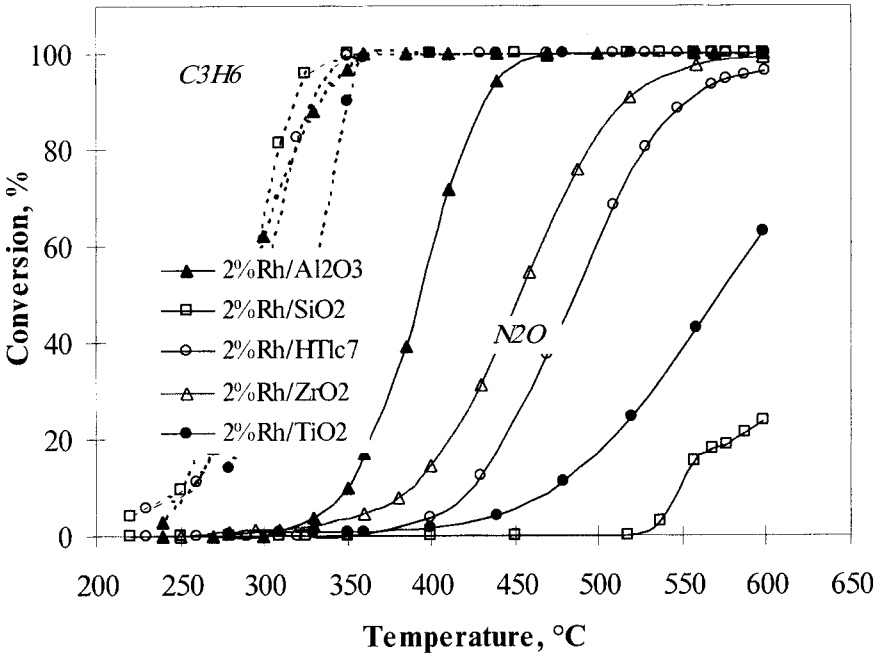


Figure 4. Conversion of N_2O (solid lines) and C_3H_6 (dashed lines) over Rh catalysts impregnated on different supports. Feed: 500 ppm N_2O, 1000 ppm C_3H_6, 5% O_2, balance He.

As a result, these oxides are the active components for the N_2O decomposition because Ru^{+3}/Ru^{+4} are effective for the N–C weakening and charge transfer during the N_2O decomposition. Therefore, we believe that C_3H_6 in the absence of O_2 reduces the Ru^{+3}/Ru^{+4} sites. These reduced sites of Ru are inactive for the N_2O decomposition.

The inhibition of the N_2O reduction over Ru/Al_2O_3, caused by the addition of propene in the feed, moderated upon the addition of 5% O_2 (figure 3). We attribute this behavior to the oxidation of propene by bulk O_2. In this way the oxidation state of the active sites remains almost unaffected by the propene presence, but competitive adsorption between N_2O, C_3H_6 and O_2 leads to lower N_2O conversions than in the experiments where N_2O or N_2O and O_2 existed in the feed.

3.3. *Effect of support on Rh-based catalysts*

The effect of the carrier on the performance of Rh-based catalysts was studied, impregnating Rh on the following supports: Al_2O_3, SiO_2, TiO_2, ZrO_2 and calcined hydrocalcite (HTlc7). We chose Rh as the active site since this metal was the most active between the alumina-based catalysts examined in figure 1. In figure 4 we present the variation of the N_2O conversion *versus* temperature curve with the type of the support. The feed in these experiments consisted of 500 ppm N_2O, 1000 ppm C_3H_6 and 5% O_2 in He. Rh/Al_2O_3 exhibited the highest activity among the catalysts of this figure. Complete conversion of N_2O to N_2 was measured over this sample at 450 °C. The corresponding temperature over Rh/ZrO_2 was 550 °C and that over Rh/HTlc7 was 600 °C. The activities of other catalysts Rh/TiO_2 and Rh/SiO_2 were lower. In accordance with the results of figure 1, the reductant was consumed at low temperatures where the N_2O reduction was negligible.

Centi *et al.* [14] studied the effect of the type of the support on noble-metal based catalysts for the decomposition of N_2O. They compared ZSM-5 with metal oxide carriers and they postulated that ZSM-5 performs as the best carrier, followed by TiO_2, Al_2O_3 and ZrO_3. They attributed differences in the activity to the variation of the Rh dispersion on different supports. Experimental results of Yuzaki *et al.* [29] agree with the results of our study.

Rh/USY and Rh/Al_2O_3 exhibited the highest activity for the N_2O decomposition. The activity of the supports varied in the following order: USY $> Al_2O_3 > ZrO_2 > CeO_2 >$ FSM $- 16 \gg La_2O_3$.

3.4. *Effect of the reducing agent*

In most of the previous experiments propene was present in the feed. However, the presence of 1000 ppm C_3H_6 in the feed decreased the N_2O conversion when 5% O_2 coexisted in the feed (figure 2). A general remark from the previous experimental data of this work is that propene was consumed at low temperatures where the conversion of N_2O is negligible. Given that propene, an unsaturated hydrocarbon, is easily burned, we chose to examine the effect of two saturated hydrocarbons (CH_4 and C_3H_8) on the N_2O reduction. These experiments were carried out over the most active

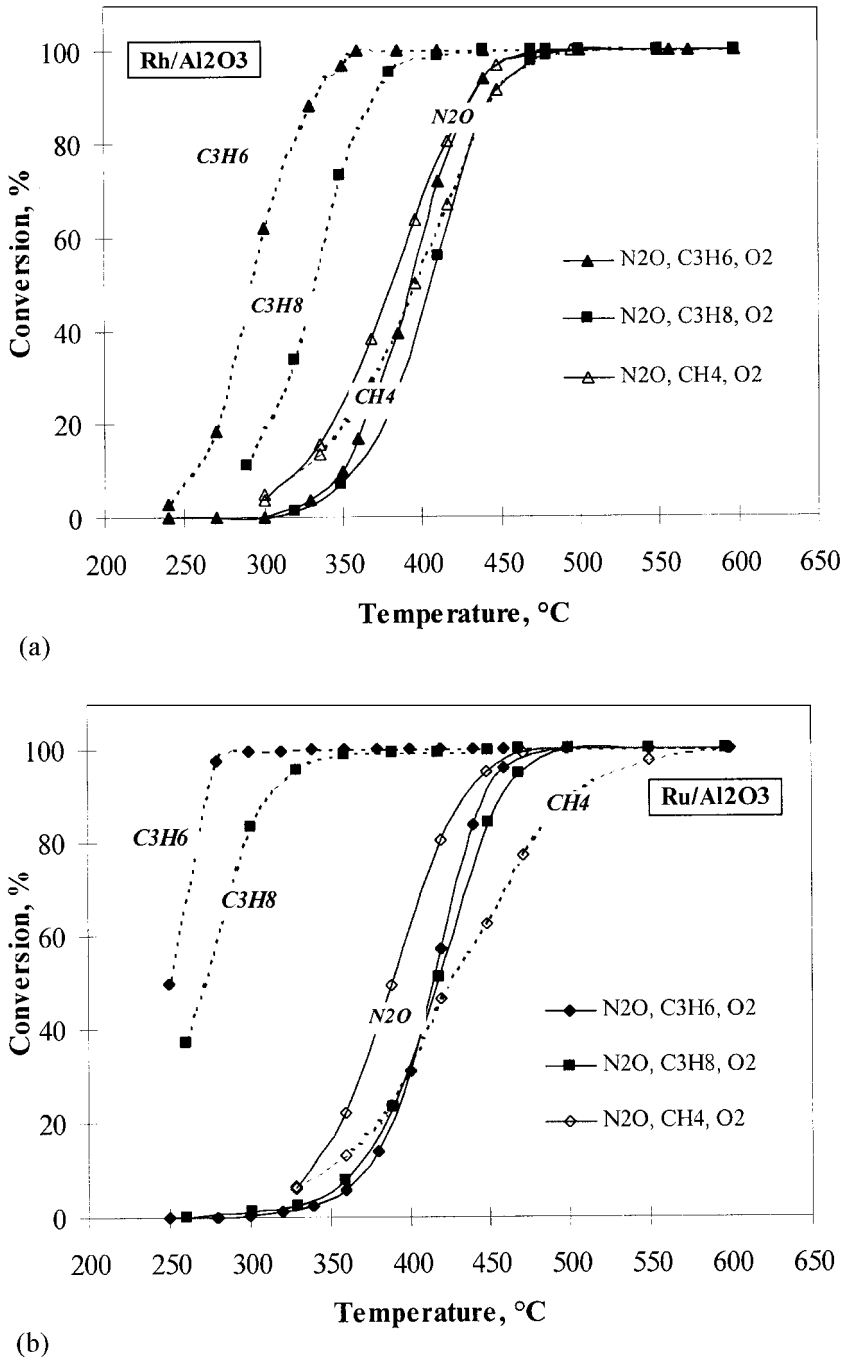


Figure 5. Effect of the type of the reducing agent on the N_2O conversion to N_2, over Rh/Al_2O_3 (a) and Ru/Al_2O_3 (b). Feed: 500 ppm N_2O, 1000 ppm C_3H_6 or C_3H_8 or CH_4, 5% O_2, balance He.

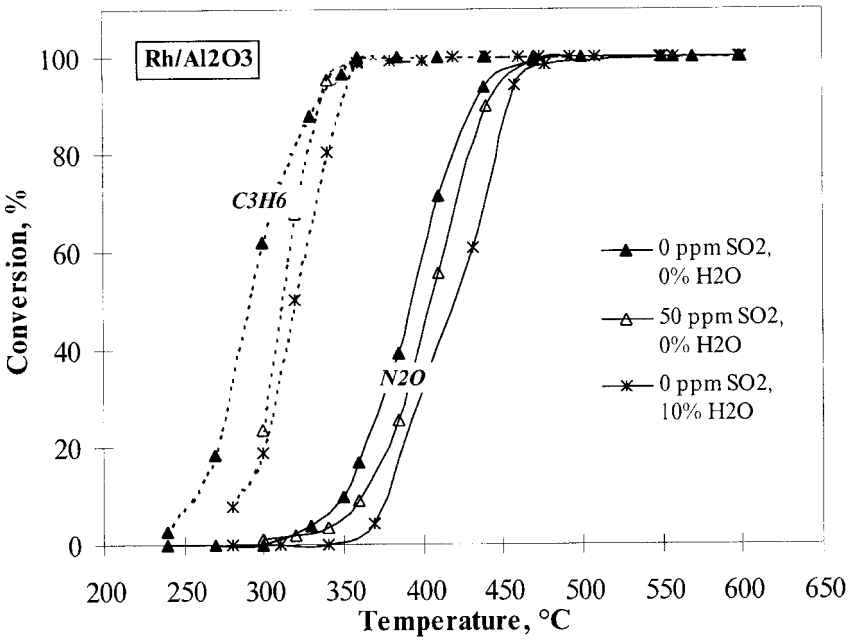
catalysts, namely Rh/Al_2O_3 and Ru/Al_2O_3, using 1000 ppm of each hydrocarbon, 500 ppm N_2O and 5% O_2.

In figure 5 we present experimental results when methane, propane and propene are present in the feed over Rh/Al_2O_3 and Ru/Al_2O_3. A small shift of the N_2O curve to higher temperatures was observed over both catalysts when propane replaced propene in the feed. On the other hand, propane was oxidized at higher temperatures than propene was. The inverse behavior was observed when methane was fed in the reactor. The light-off temperature was shifted to lower values as compared with the experiments where the other two reductants were used over both catalysts. At a given temperature the N_2O conversion was equal to or higher than that of CH_4. This implies that methane is adsorbed and burned at higher temperatures than the other two reductants. Anyway, the type of the hydrocarbon did not affect the N_2O reduction curves significantly. These results confirm our argument in section 3.1 that N_2O reduction takes place mainly

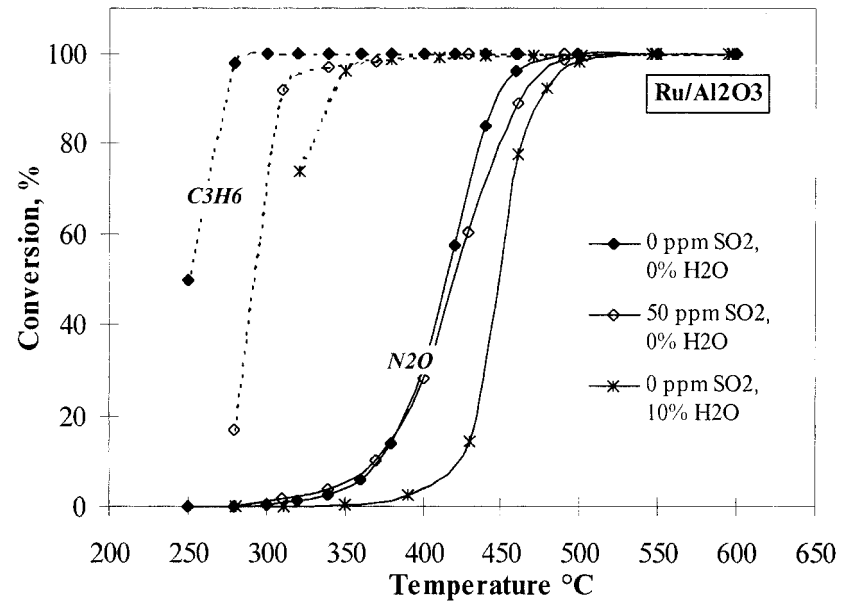
according to a decomposition reaction mechanism even in the presence of a hydrocarbon. Finally, the temperature of the hydrocarbon activation over Rh/Al_2O_3 and Ru/Al_2O_3 followed the order: $C_3H_6 < C_3H_8 < CH_4$.

3.5. SO_2 and H_2O effect on the N_2O reduction

The performance of the most promising catalysts of this study (Rh/Al_2O_3 and Ru/Al_2O_3) under realistic reaction conditions was examined by adding SO_2 and H_2O in feed that consisted of 500 ppm N_2O, 1000 ppm C_3H_6, 5% O_2 in He. We tested the influence of the H_2O and SO_2 presence initially separately, and then simultaneously. Experimental results for Rh/Al_2O_3 and Ru/Al_2O_3 are presented in figures 6(a) and 6(b), respectively. The presence of 50 ppm SO_2 in the feed caused a small shift of the N_2O curve to higher temperatures over Rh/Al_2O_3, while the same was observed over Ru/Al_2O_3 at high temperatures. The temperature where complete conversion of N_2O was measured did not



(a)



(b)

Figure 6. Effect of the presence of SO_2 and H_2O on the N_2O conversion to N_2, over Rh/Al_2O_3 (a) and Ru/Al_2O_3 (b). Feed: 500 ppm N_2O, 1000 ppm C_3H_6, 0 or 50 ppm SO_2, 0 or 10% H_2O, 5% O_2, balance He.

change significantly after the addition of SO_2 over both catalysts. These data are in agreement with experiments where N_2O was catalytically decomposed in the presence of SO_2 [14,17]. Noble metals enhance the SO_2 oxidation to SO_3, resulting in the formation of sulfates species. These species are stable on the catalytic surface up to 480–500 °C. Further increase of the reaction temperature favors their decomposition and, thus, the clean up of the catalytic surface. As a result at temperatures higher than about 480 °C the experimental data in the presence and in the absence of SO_2 are similar.

The presence of 10% H_2O in the feed inhibited the conversion of N_2O to N_2 more than SO_2 did. This inhibition was more pronounced at lower temperatures. The same trend was observed for the C_3H_6 conversion *versus* temperature curves. Similar behavior was noticed by other researchers during the catalytic decomposition of N_2O over Ru/Al_2O_3, in the presence of H_2O [13,19].

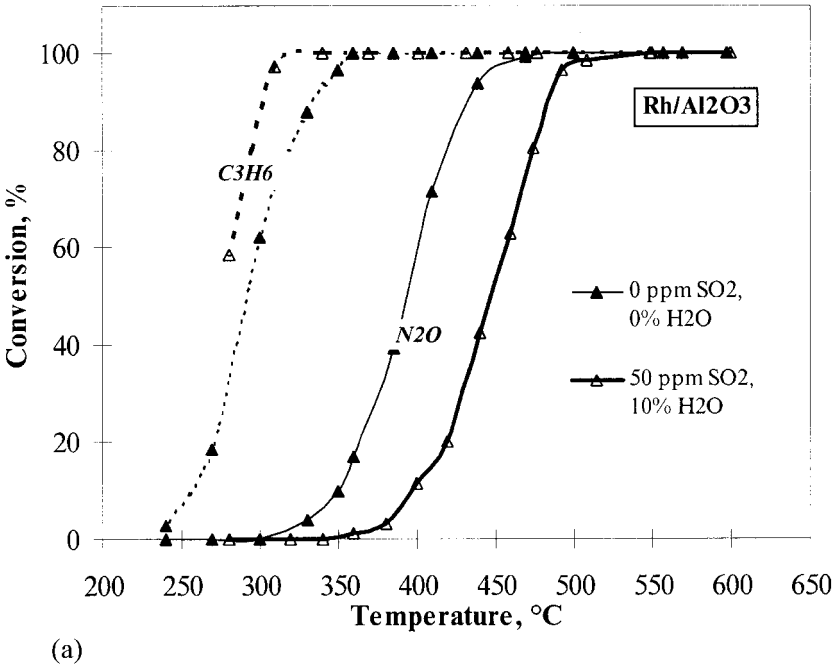


Figure 7. Effect of the simultaneous presence of SO_2 and H_2O on the N_2O conversion to N_2, over Rh/Al_2O_3 (a) and Ru/Al_2O_3 (b). Feed: 500 ppm N_2O, 1000 ppm C_3H_6, 0 or 50 ppm SO_2, 0 or 10% H_2O, 5% O_2, balance He.

Wang *et al*. [13] attributed this phenomenon to the competitive adsorption of N_2O and H_2O on the same active sites since both molecules are polar. At lower temperatures the coverage of active sites by adsorbed water reduced the number of these sites that are available for the N_2O reduction. At higher reaction temperatures the H_2O desorption was favored and the rate of the N_2O decomposition increased, reaching that of the H_2O-free experiments. Another explanation for the inhibition caused by H_2O was given by Zeng *et al*. [13]. They postulated that RuO_2 formed new phases, such as oxyhydroxides. These hydroxyl groups were retained on the surface and changed the acidity–basicity of the catalytic surface leading to the change of the electronic structure of the active RuO_2 phase and, as a result, decreased the catalytic activity.

In figures 7(a) and 7(b) we compare the conversion *versus* temperature curves for two feeds, one SO_2-free and H_2O-free and one containing both gases over Rh/Al_2O_3 and Ru/Al_2O_3, respectively. The coexistence of SO_2 and H_2O caused a shift of the N_2O conversion curves to higher temperatures of about 60 and 40 °C over Rh/Al_2O_3 and Ru/Al_2O_3, respectively. Complete conversion to N_2 was noticed above 500 °C, over both catalysts. A similar inhibition effect on the reduction of N_2O caused by coexistence of SO_2 and H_2O in the feed was observed by Centi *et al*. [3] over Fe/ZSM-5 at low temperatures, while at temperatures higher than 400 °C the catalyst maintained its initial activity. The above authors attributed this behavior to the inability of the catalyst to oxidize SO_2 to SO_3 after the initial deactivation step.

4. Conclusions

Rh and Ru supported on γ-alumina were the most promising catalysts of this study for the N_2O reduction in the presence of C_3H_6 traces and excess O_2. Complete reduction of N_2O to N_2 was measured at temperatures that varied with the composition of the feed. In the absence of O_2, C_3H_6 enhanced the N_2O reduction over Rh/Al_2O_3, but inhibited that over Ru/Al_2O_3. This was attributed to differences in the activity of fully oxidized and partially reduced metal sites. Partially reduced Rh and fully oxidized Ru are efficient catalysts for the N_2O reduction. Differences on the N_2O conversion *versus* time curves between the above two samples after the addition of O_2 was attributed to the adsorption coefficients of O_2.

Comparison of the N_2O conversion *versus* temperature curves using hydrocarbon-containing feeds showed that the type of the hydrocarbon (CH_4, C_3H_8 or C_3H_6) did not significantly affect the experimental results. Moreover, C_3H_8 or C_3H_6 was completely consumed at low temperatures where N_2O conversion was negligible. These results imply that N_2O is decomposed to N_2 rather than reduced by the hydrocarbon when O_2 is in excess in the feed.

The addition of SO_2 and/or H_2O in the feed shifted the N_2O *versus* temperature curve to higher temperatures. We attributed this behavior to the formation of sulfates that decompose at *ca*. 500 °C and to the competitive adsorption of N_2O and H_2O on the same sites.

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