Effect of SO₂ and H₂O on the N₂O decomposition in the presence of O₂ over Ru/Al₂O₃

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Abstract
Catalyst evaluation and kinetic analysis was performed on the catalytic decomposition of N₂O to N₂ over a Ru/Al₂O₃. An oxygen rich feed containing SO₂ and H₂O were used in order to examine their influence on the catalyst activity. An Al₂O₃ support was used with various Ru loadings (1–4%). No enhancement in the activity was observed for Ru loadings higher than 2%. The performance of the Ru/Al₂O₃ catalyst was tested using various pretreatment procedures. The activity of the catalysts changed with pretreatment procedure that was followed: calcinations at 600°C in inert, reducing and oxidizing atmosphere. The initial temperature of each experiment affected the catalyst activity, as well. The effect of the presence of SO₂ (0–500 ppm) and/or H₂O (0–10%) in the feed on the catalytic activity was also measured. A shift of the N₂O conversion versus temperature curve towards higher temperatures was observed when SO₂ and H₂O were added, either separately or simultaneously, into the feed. The inhibition caused by SO₂ was attributed to the formation of sulphates while that caused by water to the competitive chemisorption of H₂O and N₂O on the same active sites. Finally, kinetic and TPD studies showed that N₂O is catalytically decomposed to N₂ both in absence and presence of poisonous gases.

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1. Introduction

Nitrous oxide (N₂O) contributes to the destruction of ozone in the stratosphere and it is considered as a strong greenhouse gas [1,2]. The major industrial source of N₂O is the production of nitric acid (400 kt N₂O per year), which is a key raw material in the fertilizer industry [3]. N₂O is also produced during the synthesis of adipic acid, caprolactam, glyoxal, and from combustion processes of fossil fuels, biomass, and waste.

Among different anthropogenic emissions those that can be reduced in the short-term are the ones associated with combustion processes and chemical production [1,2]. Up to now the European Union has not set specific emission limits for N₂O, however, it is expected to do so in the near future. Thus, there is a strong need for the development of new efficient and economical technologies, which will ensure the elimination of N₂O from flue gases.

The catalytic decomposition and the selective catalytic reduction (SCR) of N₂O to N₂ are two candidate technologies, which can be applied to reduce the N₂O emissions. The selective catalytic reduction of N₂O has been studied over copper (Cu) and iron (Fe) deposited on various zeolites (ZSM-5, MFI) [2,4–9].

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Both catalysts exhibited high activity under ideal reaction conditions (absence of poisonous gases). Fe/ZSM-5 maintained most of its initial activity even after the addition of water (H2O) into the feed. The H2O presence caused a shift of the N2O conversion versus temperature curve towards higher temperatures over Cu/ZSM-5. Centi and Vazzana [7] examined the tolerance and the durability of Fe/ZSM-5 using a feed that simulated flue gases. Their experimental results showed that about 60% of the N2O was reduced to N2 for more than 600 h in the presence of 500 ppm sulfur dioxide (SO2). SO2 was not oxidized to SO3 over the catalyst and this caused the tolerance of this catalyst to the SO2 presence, according to the above authors. The N2O reduction by CO [10] or CH4 [11] has been examined in the absence of O2. NH3, as well, has been used as the reducing agent [12–14]. However, the presence of 3% O2 caused a significant inhibition of the reaction.

The catalytic decomposition of N2O has been studied to a greater extent than SCR over a large variety of catalysts, which included supported and unsupported metals, pure and mixed oxides, and zeolitic systems [1,2]. Supported oxides are more effective in practical applications due to the higher dispersion of active sites and the higher specific surface area of the support. In most works alumina was used as carrier and Pd, Cu, Co, Mn, Rh, Ru, Fe, Cr, etc. as active sites. Catalysts based on cobalt, copper, ruthenium and rhodium exhibit high catalytic activity for the N2O decomposition [15–22]. In our previous communication [22], the performance of various catalysts deposited on γ-alumina, was examined. The experimental results showed that both Rh/Al2O3 and Ru/Al2O3 were active catalysts leading to complete reduction of N2O to N2 at high temperatures. The activity of other catalysts studied in the same work (Fe/Al2O3, Pd/Al2O3, In/Al2O3, Co/Al2O3) was significantly lower. Li and Armor [16,17] concluded that Rh- and Ru-exchanged ZSM-5 are the most active catalysts for the N2O decomposition. These authors also reported that the activity of the Ru-ZSM-5 catalyst dramatically declined in the presence of oxygen, which was attributed to catalyst deactivation caused by oxygen, presumably due to the formation of ruthenium oxides. Chang et al. [19] showed that Ru-HNaUSY is a highly active catalyst for the N2O decomposition at low temperatures (120–200 °C). Kinetic rate measurements revealed that the decomposition of N2O over Ru-HNaUSY and Ru-NaZSM-5 followed a first order reaction rate with respect to the N2O partial pressure, and had a negative-power law dependence on the oxygen partial pressure. This strong oxygen inhibiting effect suggested that the desorption of oxygen was the rate limiting step in the N2O decomposition. Furthermore, Chang et al. [20] studied the effect of Ru loading on the kinetics of the reaction over the Ru-NaZSM-5 zeolite. Higher Ru-loadings led to lower turnover frequency rates and to higher apparent activation energy. They concluded that high and low Ru-loadings resulted in active catalysts in the presence and absence of excess oxygen, respectively.

Zeng and Pang [23] examined the N2O decomposition reaction over Ru/Al2O3. They observed that the surface area of Ru/Al2O3 decreased with the increase of the metal loading and that O2 exhibited negligible inhibition effect. The presence of CO2 in the feed modified the surface acidity–basicity, while H2O had a retardation effect, which was attributed to the change of the chemical constituent and, thus, of the acidity–basicity of the catalyst surface. Wang and Zeng [24] studied the decomposition of N2O over Ru/Al2O3 catalysts. Excellent catalytic activity was measured for both dry and wet N2O feeds. Pinna et al. [25] examined the N2O decomposition over Ru supported on ZrO2. They concluded that the oxidized samples exhibited higher conversion than the reduced ones. Surface Ru6+ interacted N2O. N2O acted as an oxidant of the ruthenium reduced sites and as a reductant of the overoxidized sites. Finally, Kawi et al. [26] studied the same reaction over a Ru/MCM-41 catalyst and investigated the effect of the following factors on the catalytic performance of the catalyst: Ru precursors, amount of Ru loading on the support, impregnation method, presence of oxygen, carbon monoxide (CO) and moisture in the feed stream. Ru/MCM-41 catalyst prepared from Ru(OH)3 was the most active for the catalytic decomposition of N2O. Moreover, the catalyst activity was significantly enhanced when CO was introduced into the feed stream. On the contrary, the presence of moisture and oxygen slightly decreased the catalyst activity, due to the competitive adsorption between these species and N2O for the catalytic sites.
The effect of compounds that typically exist in flue gas, such as O$_2$, CO, CO$_2$, S O$_2$, and H$_2$O on the activity of catalysts used for the N$_2$O decomposition has been studied in previous works. However, the effect of these gases on the reaction mechanism was not examined. In this work we studied the performance of Ru/Al$_2$O$_3$, a catalyst that exhibit high N$_2$O reduction rate when the feed is poison-free, in the presence and the absence of SO$_2$ and H$_2$O in an oxygen-rich atmosphere. We measured the activity and we calculated kinetic and adsorption data for the N$_2$O decomposition. Finally, we used our experimental results to propose a reaction mechanism for the N$_2$O decomposition.

2. Experimental

2.1. Materials

γ-Alumina extrudates supplied by Engelhard (sample code: Al-3992 E 1/8") were used as the support of the catalyst. The extrudates were crushed and sieved in order to be separated into particles of size 180–355 μm. The dry impregnation technique was employed for the impregnation of Ru on the γ-alumina carrier. The impregnation of the support was performed using a RuCl$_3$·xH$_2$O solution provided by next chimica. The catalyst was dried at 120 °C for 2 h and calcined in air at 550 °C for 4 h prior to the reaction [27]. The metal loading was varied from 1 to 4 wt.%.

2.2. Catalyst characterization

The Ru/alumina catalyst was characterized by using the nitrogen (N$_2$) adsorption, the X-ray diffraction (XRD) and the EDS techniques. The N$_2$ adsorption data measured in an Autosorb-1 (Quantachrome) apparatus were used for the calculation of the BET surface area of the samples, while the pore structure of the samples was determined by an Autopore II (Micrometrics) porosimeter. Crystallographic information was collected using the powder XRD technique. The diffraction intensity−2θ spectra were measured by a Siemens D 500/501 with Cu Kα radiation (λ = 1.54178 Å) at a scanning rate of 0.04° over 2θ. Finally, energy dispersive X-ray spectrometer measurements were performed using a JEOL JSM-6300 spectrometer.

2.3. Reaction/analysis system

The experiments were carried out in a quartz, fixed-bed, micro-reactor (0.018 m i.d.) [27]. The catalyst was loaded onto a fine-quartz fritted disk and the reaction temperature was continuously monitored by a thermocouple inserted inside the catalyst bed. A second thermocouple, located next to the fritted disk, was used to measure the temperature of the effluent gases. The reaction unit was equipped with mass flow controllers and pressure indicators for the accurate control of the flow and partial pressure of each reactant. Product analysis was performed with a series of on-line gas analyzers and a gas chromatograph (Hewlett-Packard 6890 series) equipped with TCD and FID [27]. A molecular sieve 13× column and a HayeSep N column were used for the separation of the inorganic and organic species, respectively. The on-line analyzers were: a chemiluminescence NO/NO$_2$/NO$_x$ analyzer (42C-HL, Thermo Environmental), a non-dispersive infrared (NDIR), a CO and CO$_2$ analyzer (NGA 2000, Rosemount), a magnetopneumatic O$_2$ analyzer (MPA-510, Horiba), a N$_2$O analyzer (VIA-510, Horiba) and a SO$_2$ analyzer (NGA 2000, Rosemount). The signals received from the analyzers were continuously recorded in a PC.

2.4. TPD procedure

Temperature programmed desorption (TPD) studies of the N$_2$O adsorption experiments were carried out in a quartz reactor using the same procedure described by Gao and Au [28]. The sample (0.5 g) was placed in a quartz reactor of 0.007 m i.d., where was first calcined in situ at 700 °C for 1 h under a He flow (20 cm$^3$/min) and then cooled down to room temperature. Next, the sample was kept in an N$_2$O-containing flow (20 cm$^3$/min) for 1 h at 300 °C and, subsequently, cooled again down to room temperature. After being He-purged at room temperature for 1 h, the sample was heated to 600 °C in helium (20 cm$^3$/min) with a heating rate of 10 °C/min. The reactor exit was connected to the gas analysis system. The variation of the gas concentration with the reaction temperature was continuously recorded.
3. Results and discussion

3.1. Catalyst characterization

The Ru-impregnated Al₂O₃ was characterized by surface area measurements, in order to investigate the effect of pretreatment, Ru loading and presence of SO₂ in the gas feed. The surface of γ-Al₂O₃ was initially 180 m²/g. After impregnation with Ru, the surface area of the fresh material increased to about 192 m²/g. The most probable pore size was equal to 110 Å.

After pretreatment (1 h under He flow at 600 °C), the surface area of the sample decreased to 135 m²/g (i.e. a 25% reduction). This was attributed to thermal sintering. The surface area of a fresh 4% Ru/Al₂O₃ catalyst was 181 m²/g. Consequently, the deposition of Ru did not modify the internal surface area of the catalyst.

Before evaluating the effect of the presence of SO₂, the resulting surface area of a 2% Ru/alumina sample after reaction without poisons was measured. It was found that, when the catalyst was exposed to the reacting mixture, a sharp decrease of the surface area occurred (i.e. 89 m²/g). The presence of SO₂ in the feed caused an increase of the surface area of the sample. A sample exposed to a gas feed containing 50 ppm SO₂ had a surface area equal to 142.9 m²/g, while the surface area of the same sample exposed to 200 ppm SO₂ was equal to 140.3 m²/g. Thus, it was clear that the surface area increased in the presence of SO₂ and was almost independent of SO₂ concentration. This specific increase could be attributed to the resulting decrease of the pore size (90 Å) as compared to the pore size of the fresh sample.

The surface Ruthenium species on γ-Al₂O₃ were identified by X-ray diffraction (XRD). RuO₂ dominated on the catalyst surface, as expected, when the catalyst was pretreated with He or/and O₂ gas mixtures. When the catalyst was pretreated with H₂/He, only reduced Ru was identified on the surface. In all reacted samples ruthenium was in the form of RuO₂, this was attributed to the presence of 5% O₂ in the gas feed. When the feed contained SO₂ we did not observe the formation of Al₂(SO₄)₃ on the catalytic surface. However, the presence of sulfates with concentration lower than the resolution of the XRD technique cannot be excluded.

Finally, the EDS analysis showed that Ru was homogeneously dispersed on the catalyst surface over all samples (fresh and used). When the feed contained 50 or 200 ppm SO₂ we observed that sulfur was sparsely or homogeneously dispersed on the catalyst surface, respectively.

3.2. Effect of Ru loading

We varied the Ru loading on γ-alumina (1, 1.5, 2, 2.5, 3, 4% Ru/Al₂O₃) to choose the optimum loading for the N₂O decomposition reaction in the presence of excess oxygen. Screening tests were carried out for the N₂O decomposition reaction using the following feed: 500 ppm N₂O and 5% O₂ in He (catalyst weight: 1 g, \( F = 500 \text{ cm}³/\text{min} \)). The N₂O conversions versus the reaction temperature curves over the Ru-based catalysts are presented in Fig. 1. The temperatures where the curves become sharp do not necessarily decrease with the increase of the Ru loading. For a given conversion, the catalyst with the lowest decomposition temperature was the 2.5% Ru/Al₂O₃. The experimental curves for Ru loadings in the range of 1.5–3% almost coincide. The interpretation of these results requires metal dispersion measurements that were not carried out in this work. Increase of the metal loading may lead to the aggregation of metal particles and thus, to lower dispersion.

Zeng and Pang [23] studied the effect of Ru loading on the same reaction in the absence of O₂. They noticed that the surface area of Ru/Al₂O₃ decreased with the increase of the metal loading. The optimum metal loading was equal to 0.2% (one order of magnitude lower than the results of the present study). However, the presence of oxygen affects the reaction mechanism that leads to the N₂ formation from N₂O. Kawi et al. [26] also examined the effect of Ru loading on MCM-41. The activity initially increased with the Ru loading (0.5–5 wt.%) and subsequently decreased as Ru loadings further increased from 5 to 10 wt.%. As a result, the maximum conversion of N₂O was measured when 5% Ru was deposited on MCM-41. We chose to use the 2% Ru/Al₂O₃ in the experiments that are presented in the following part of this work because the metal loading is moderately high and the activity is comparable to that of samples with higher metal loading.
3.3. Effect of the catalyst’s pretreatment procedure

The treatment of the catalyst prior to reaction affects its activity. As a result, we followed three types of catalyst pretreatment. The feed during this stage was either pure He, or 5% H₂ in He, or 5% O₂ in He; the flow rate was 500 cm³/min, the temperature was 600 °C and the duration of the treatment was 1 h. Catalyst samples were evaluated both in the absence and presence of poisonous gases.

Fig. 2 shows the effect of temperature on the activity of Ru/alumina for the N₂O decomposition reaction in the presence of excess oxygen, for the three types of pretreatment described earlier. These experiments were performed using a different temperature sequence. Specifically, the initial temperature was either the highest or the lowest of the experiment, followed by a gradual decrease or increase, respectively, of the reaction temperature. The following reaction feed was used throughout all experiments: 500 ppm N₂O, 5% O₂ in He (catalyst weight: 1 g, F = 500 cm³/min).

A sigmoid-type conversion versus temperature curve was observed in all experiments. The most active catalyst was the one pretreated with He and when we started the experiment at the highest temperature, while the less active catalyst was the one pretreated with O₂ and when we started at the lowest temperature. When the sample was pretreated with H₂ the variation of the N₂O conversion with the temperature was not affected by the starting temperature. The opposite was observed when the other two types of pretreatment were employed. If we combine the two experimental curves (temperature increase–decrease in Fig. 2) for a given type of pretreatment we observe the formation of a hysteresis-type dependence. In these experiments for a given temperature higher conversions were measured when the experiment started at the highest temperature.
Fig. 2. Effect of the pretreatment procedure on the $\text{N}_2\text{O}$ conversion over Ru/Al$_2$O$_3$. Feed: 500 ppm $\text{N}_2\text{O}$, 5% $\text{O}_2$, balance He. Flow rate: 500 cm$^3$/min, catalyst weight: 1 g.

The same series of experiments was repeated in the presence of poisonous gases (addition of 50 ppm $\text{SO}_2$ and 10% $\text{H}_2\text{O}$ to the feed). Fig. 3 depicts the effect of temperature on the activity of the Ru/alumina catalyst for different pretreatments. In most of the experiments of this figure we observe a turning point, i.e. a temperature in the range of 450–470$^\circ$C, where the slope of the conversion versus temperature curve changes abruptly. At temperatures higher than this turning point we observe that the slope of the experimental curves drops and complete conversion is reached at significantly higher temperatures when the experiment starts at the lowest temperature. In all experiments of Fig. 2 and in the experiments of Fig. 3 that start at the highest temperature complete conversion is reached immediately after the turning point. Moreover, the experimental curves presented in Fig. 3 are intercepted, while the corresponding curves in Fig. 2 are parallel to each other.

Pinna et al. [25] studied the effect of the catalyst pretreatment procedure on the catalytic decomposition of $\text{N}_2\text{O}$ over Ru/ZrO$_2$. In this work, the oxidized samples exhibited higher conversions than the reduced ones. The formation of NO in the gas phase was detected. The authors proposed that $\text{N}_2\text{O}$ decomposition mainly occurred on the exposed reduced Ru sites. Finally, they concluded that $\text{N}_2\text{O}$ acted as an oxidant on the reduced sample and as a reductant of the fully oxidized ruthenium.

In our experiments, no NO molecules were detected during the reaction. When the experiment started at high temperatures the feed $\text{O}_2$ oxidized rapidly any reduced Ru sites and this is illustrated to the small variations in the conversion versus temperature curves presented in Figs. 2 and 3. It must be mentioned that XRD analysis showed that Ruthenium oxide existed on all reacted and unreacted samples except in the case of unreacted samples pretreated with $\text{H}_2$, where metallic Ru prevails the catalyst surface.
3.4. Effect of poisonous gases on the activity of N\textsubscript{2}O decomposition in excess oxygen over Ru/Al\textsubscript{2}O\textsubscript{3}

The presence of gases that do not participate in the N\textsubscript{2}O decomposition, such as SO\textsubscript{2} and H\textsubscript{2}O on the kinetics and the mechanism of reaction was examined. We initially studied the effect of each of the above compounds on the extent of conversion separately and then in combination.

Vapor water typically exists in the flue gases. Experiments were, thus, carried out using a feed gas with the following composition: 500 ppm N\textsubscript{2}O, 5% O\textsubscript{2} and 0, 5 and 10% H\textsubscript{2}O in He. The reactor loading was 1 g of 2% Ru/Al\textsubscript{2}O\textsubscript{3} and the total flow rate was 500 cm\textsuperscript{3}/min. The addition of water shifted the experimental curves to higher temperatures (approximately 75 °C) as it is shown in Fig. 4. The concentration of H\textsubscript{2}O in the feed did not affect the activity of the catalyst. Similar behavior was also observed by other researchers who studied the catalytic decomposition of N\textsubscript{2}O over Ru/Al\textsubscript{2}O\textsubscript{3} in the presence of water [23,24]. We attributed the inhibition caused by the water presence in the feed to the competitive adsorption of H\textsubscript{2}O with N\textsubscript{2}O on the catalyst surface.

We performed step changes in the water concentration (0 or 10%) at a constant temperature (480 °C) and under reaction conditions identical to those used in Fig. 4. The addition of 10% water after 1 h reaction in dry conditions caused initially a sharp decrease of the N\textsubscript{2}O conversion followed by a rise up to approximately 90%. When the feed was switched to dry the conversion further increased to 95% and remained constant even after the addition of 10% water. The same cycle was repeated once more and the conversion remained in the vicinity of 100% in the presence and the absence of water. Therefore, at this relatively high temperature the presence of water practically does not affect the N\textsubscript{2}O conversion.
Figure 4. Effect of the inlet H$_2$O concentration on the N$_2$O conversion over Ru/Al$_2$O$_3$. Feed: 500 ppm N$_2$O, 5% O$_2$, 0–10% H$_2$O, balance He. Flow rate: 500 cm$^3$/min, catalyst weight: 1 g.

The presence of water in the feed does not always affect the extent of the reaction [1]. Given that the adsorption of water is exothermal, inhibition caused by water is observed at low temperatures, whereas the activity is not affected at higher temperatures. As a result, at low temperatures, competing adsorption of H$_2$O and N$_2$O takes place, since they are both polar molecules and use the oxygen end of the molecules to strike a vacant Ru site [23,24,26]. On the other hand, high temperatures favor hydrothermal deactivation [1]. The reaction between the solid catalyst and H$_2$O can lead to modification of the initial active catalytic phase [23,24]. Specifically, under wet reaction conditions we may have the formation of oxyhydroxides (RuO$^+$OH$_2$ and (RuO$_2$)OH$_2$$^+$) from the RuO$_2$ (or RuO$_x$). The presence of water in the feed may change the surface acidity–basicity of the catalyst. The oscillations in the N$_2$O formation observed in Fig. 5 can be attributed to redox cycles taking place on the catalytic surface. Another explanation for the same
phenomenon is the periodic evaporation of water that accumulates on the catalytic surface.

SO$_2$ is frequently present in the flue gases derived from combustion and chemical production plants [2]. We, therefore, performed a series of experiments aiming at the SO$_2$ effect on the extent of the N$_2$O decomposition reaction at different temperatures ranging from 200 to 600$^\circ$C. The N$_2$O conversion versus temperature curves over a 2% Ru/Al$_2$O$_3$ for 0, 50, 100 and 200 ppm SO$_2$-containing feed gas streams are presented in Fig. 6. It is evident that the presence of SO$_2$ caused a dramatic decrease of the N$_2$O decomposition. An increase in the inlet SO$_2$ concentration leads to a shift of the experimental curve to higher temperatures. This shift is higher from 0 to 100 ppm SO$_2$ as compared to a further concentration increase. Our experimental results agree with previous works that examine the catalytic N$_2$O decomposition in the presence of SO$_2$ [2,29,30].

In the experiment presented in Fig. 7, we introduced step changes using a variable inlet SO$_2$ feed concentration. The duration of each step was 1 h and the temperature 480$^\circ$C. A significant decrease was observed when we inserted SO$_2$ in the feed gas, while a 50% reduction in the N$_2$O conversion was measured, when 200 ppm SO$_2$ were fed, compared with the corresponding conversion in the case of 100 ppm SO$_2$. Partial recovery of the activity was noticed in the successive SO$_2$-free steps. The conversion dropped to about 20% when the feed contained 500 ppm SO$_2$.

The sensitivity of Ru/Al$_2$O$_3$ to the feed SO$_2$ is presented in Fig. 8, where the effect of 50 ppm SO$_2$ on the activity is measured for 24 h of continuous operation at 490$^\circ$C. The conversion was initially 100%. One and a half hour later, the conversion started to gradually decrease until it reached the final value (about 27%) after 11 h of operation. Afterwards, the conversion remained constant until the end of the experiment.

When SO$_2$ is present in the feed, most of the catalysts used for N$_2$O decomposition rapidly deactivate,
since they are also active for the oxidation of SO$_2$ to SO$_3$ [1]. SO$_3$ then reacts with the catalyst to form a stable sulfate (in this case aluminum sulfate), which inhibits the catalyst activity [2]. These species are stable on the catalytic surface up to 480–500 °C. Further increase of the reaction temperature favors their decomposition and, consequently, the cleanup of the catalytic surface. Therefore, catalytic system can tolerate the SO$_2$ presence in the feed only at significantly high temperatures. When operation at high temperatures is not feasible reduction of sulfates may lead to partial or complete regeneration of the initial catalytic activity.

In most flue gases SO$_2$ and H$_2$O coexist. Therefore, we performed a series of experiments where the feed contained both SO$_2$ and H$_2$O. We chose to use a constant H$_2$O concentration of 10% and we varied the SO$_2$ concentration in the range of 0–500 ppm. The variation of the N$_2$O conversion with the reaction temperature is shown in Fig. 9. The co-existence of SO$_2$ and H$_2$O caused a shift of the N$_2$O conversion curves towards higher temperatures that increased with the SO$_2$ concentration. The inhibition caused by both gaseous compounds is not cumulative: for example, the addition of 10% water caused a 75 °C shift of the conversion curve (Fig. 4), while the addition of 50 ppm SO$_2$ resulted in a 70 °C shift (Fig. 6). The simultaneous addition of SO$_2$ and H$_2$O in the feed shifted the decomposition curve towards higher temperatures by 85 °C (Fig. 9). The catalyst activity in the presence of the highest SO$_2$ concentration (500 ppm) was limited to temperatures higher than 500 °C. We have also performed step changes and transient tests in the presence of both SO$_2$ and H$_2$O and the behavior was similar as in the previous cases where we examined separately the effect of SO$_2$ and moisture.
3.5. Kinetic and mechanistic analysis of N$_2$O decomposition over Ru/Al$_2$O$_3$

Preliminary kinetic experiments were performed in order to determine the appropriate set of experimental parameters that would ensure catalyst evaluation for the decomposition of N$_2$O based on intrinsic kinetic measurements. We varied the space-time and the catalyst particle size to determine any possible influence of external and internal mass transfer limitations on the catalytic activity, respectively. Variable space-time experiments were performed at 395 $^\circ$C, and a W/F value equal to 0.018 g cm$^{-3}$ s was selected which corresponded to a catalyst weight of 0.25 g and a feed flow of 800 cm$^3$/min. Furthermore, in our previous work [31] we measured no significant influence of internal mass transfer limitations on the catalytic activity of samples with particle size <355 μm. Finally, the apparent activation energy of the reaction was calculated equal to 46.7 ± 4.3 kcal/mol, a value similar with that of previous studies [1].

The effect of reactive gas concentration on the N$_2$O decomposition was examined, keeping the other reaction parameters, such as reaction temperature and space velocity constant. The reaction temperature was to ensure “differential” reaction kinetics (conversion less than ca. 20%). As a result, the expressions developed in this work may not apply at higher temperatures. We initially varied the inlet N$_2$O concentration in the range of 150–1500 ppm. The N$_2$O decomposition rate over Ru/Al$_2$O$_3$ was measured at 385°C. We used these experimental results to calculate the apparent reaction order with respect to the N$_2$O concentration. We also varied the inlet O$_2$ concentration in the range of 0.5–10% over the same catalyst and at the same temperature. The apparent order of reaction for the N$_2$O and the O$_2$ concentration was 1.17 ± 0.03 and −0.27 ± 0.02, respectively. We developed the following reaction rate expression

\[ \text{Rate} = k [\text{N}_2\text{O}]^{1.17} [\text{O}_2]^{-0.27} \]
for the N\(_2\)O decomposition in the presence of oxygen over Ru/Al\(_2\)O\(_3\).

\[
r(\text{N}_2\text{O}_{\text{dec}}) = k_{\text{dec}} \left[ \text{N}_2\text{O} \right]^{1.17} \left[ \text{O}_2 \right]^{-0.61}
\]

(1)

The N\(_2\)O decomposition is approximately proportional to the N\(_2\)O concentration, while O\(_2\) inhibits the decomposition. The latter agrees with the results of Zeng and Pang\([23]\) over the same catalyst (Ru/Al\(_2\)O\(_3\)).

We repeated the above kinetic experiments in the presence of SO\(_2\) and H\(_2\)O. A typical feed composition of 500 ppm N\(_2\)O, 5% O\(_2\), 50 ppm SO\(_2\) and 10% H\(_2\)O in He were employed along with a catalyst weight of 0.25 g and a total flow of 800 cm\(^3\)/min (W/F = 0.018 g s/cm\(^3\)). The apparent activation energy of the N\(_2\)O decomposition reaction was equal to 45.8 \pm 5.7 kcal/mol. The presence of poisonous gases slightly decreased the value of the activation energy.

We varied the inlet N\(_2\)O concentration in the range of 250–3000 ppm and measured the N\(_2\)O decomposition rate over Ru/alumina at 410 °C. These experimental results were used to calculate the apparent reaction order that was equal to 1.19 \pm 0.16. The same procedure was used for O\(_2\) concentration in the range of 1–10% at the same temperature. The apparent reaction order was calculated to be nearly zero. However, during these experiments small fluctuations were observed in the reaction rate. This was attributed to adsorption/desorption of the feed gases on the catalyst.

Furthermore, the effect of different inlet SO\(_2\) concentration (50–500 ppm) on the N\(_2\)O decomposition over Ru/Al\(_2\)O\(_3\) at 410 °C was measured. The apparent reaction order for SO\(_2\) was equal to \(-0.61 \pm 0.24\). We combined the above experimental data to develop a kinetic expression for the N\(_2\)O decomposition over Ru/Al\(_2\)O\(_3\) in the presence of O\(_2\), SO\(_2\), and H\(_2\)O.

\[
r(\text{N}_2\text{O}_{\text{dec}}) = k_{\text{dec}} \left[ \text{N}_2\text{O} \right]^{1.19} \left[ \text{SO}_2 \right]^{-0.61}
\]

(2)

In agreement with expression (1) the N\(_2\)O decomposition is approximately proportional to the inlet N\(_2\)O concentration.
concentration. The inhibition effect of the inlet O₂ concentration in expression (1) is replaced by the one of SO₂. This can be attributed to the rapid SO₂ oxidation to SO₃ over the Ru sites. Therefore, oxygen derived from the bulk phase and oxygen derived from the N₂O decomposition is consumed for the SO₂ oxidation. As a result, active sites are no longer available for the N₂O decomposition. In order to fit all the above data we used the least squares method and we achieved always a correlation coefficient ($R^2$) value higher than 0.98.

In the N₂O TPD studies, we used the procedure described by Gao and Au [28]. Fig. 10 shows the evolution of N₂O desorbed from γ-Al₂O₃ and Ru/Al₂O₃ in the presence and absence of 5% oxygen. Initially, the N₂O sorption capacity of the support was studied. The feed consisted of 0.5% N₂O in He during the sorption stage ($T = 300^\circ$ C) and of pure He during the desorption stage of the experiment. One N₂O peak was observed at 237°C. The overall amount of the desorbed N₂O was calculated integrating the desorption peak and it was about $21.6 \times 10^{-6}$ mol. The N₂O desorption curve over Ru/Al₂O₃ exhibited a first peak at $147^\circ$ C that was attributed to Ru sites and a second peak at $200^\circ$ C attributed to the support. This implies that the bond between the N₂O and the support was stronger than between the N₂O and Ru. The total amount of desorbed N₂O in both peaks was $12.6 \times 10^{-6}$ mol. At higher temperatures, a small peak corresponding to NOₓ desorption was also detected. Following that, 5% O₂ was added to the N₂O/He sorption mixture and the TPD experiment was repeated (Fig. 10). Over the alumina sample, a peak was observed at 295°C ($29.9 \times 10^{-6}$ mol), while the corresponding peak in the absence of O₂ appeared at lower temperatures. The same experiment carried out over Ru/Al₂O₃ revealed again two peaks: the first at 220°C attributed to the presence of Ru and the second at 295°C attributed to the support. The overall amount of desorbed N₂O was $16 \times 10^{-6}$ mol. It is probable that N₂O is sorbed over
electron deficient Ru sites that exist on the catalyst at ambient temperatures.

TPD experiments were also performed in order to study the simultaneous adsorption/desorption of N₂O and SO₂ in the presence of O₂ (Fig. 11). Over γ-Al₂O₃, two peaks corresponding to N₂O and one sharp peak corresponding to NOₓ were noticed. These results indicated the presence of two types of adsorbed N₂O: one weakly (at \( T = 222^\circ C \)) and one strongly-bonded (at \( T = 318^\circ C \)). The total amount of adsorbed N₂O was equal to \( 30.8 \times 10^{-6} \) mol. On the other hand, NOₓ desorbed at \( 436^\circ C \) exhibiting a very sharp curve (44.4 \( \times 10^{-6} \) mol). It is interesting that only NO (no NO₂) was desorbed. This implies that, in the presence of SO₂, N₂O formed NO over the support. Over Ru/Al₂O₃, two consecutive N₂O peaks were observed, the first one on Ru at \( T = 195^\circ C \) and the second one on alumina at \( T = 295^\circ C \). Moreover, the total amount of desorbed N₂O (21.7 \( \times 10^{-6} \) mol) was lower than over the support. A small peak corresponding to NOₓ was detected at higher temperatures (i.e. \( T = 505^\circ C \)). Comparing the N₂O desorption data for the SO₂-free and SO₂-containing feeds over alumina, it was concluded that the presence of SO₂ weakened the N₂O-Ru bond, while at the same time strengthened the N₂O-alumina. Finally, over γ-Al₂O₃, when SO₂ was added, an extensive release of NO strongly bonded on the surface was observed, which denotes that the presence of SO₂ favored the oxidation of N₂O to NO over γ-Al₂O₃. Obviously, these oxidation sites were not present when Ru was impregnated on alumina because no NOₓ release over Ru/Al₂O₃ was observed.

In our reaction kinetics studies we developed expression (1), where the N₂O decomposition rate was proportional to the inlet N₂O concentration. This implies that N₂O was molecularly adsorbed on the catalyst surface in accordance to our TPD experiments. In the same reaction rate expression the inlet oxygen concentration exhibited a moderate negative effect on the decomposition rate. This inhibitive effect was also reported by Zeng and Pang [23] and can
be attributed to the reversible dissociative adsorption of oxygen, either directly or via molecular adsorption of oxygen, as proposed to occur over metal surfaces [1]. Moreover, the negative reaction order of oxygen denotes that oxygen desorption might be the rate determining step of the reaction. The importance of the catalyst oxidation state was also demonstrated in experiments where the catalyst was pretreated under different conditions (Figs. 2 and 3). Thus, for low nitrous oxide coverage and high partial pressure of oxygen, the following reaction scheme is proposed, in which the desorption of oxygen (steps 6 or 7) probably determine the overall reaction rate [1].

\[
\begin{align*}
N_2O + X & \leftrightarrow N_2O - X \\
N_2O - X & \rightarrow N_2 + O - X \\
O_2 + X & \rightarrow O_2 - X \rightarrow 2O - X \\
2O - X & \leftrightarrow O_2 + 2X \\
N_2O + O - X & \leftrightarrow N_2 + O_2 + X
\end{align*}
\]

The above reaction scheme involves an adsorption step of N₂O at the active center (Ru-site) (Eq. (3)), followed by a decomposition step that gives rise to the formation of N₂ and a surface oxygen (Eq. (4)). This surface oxygen can desorb either by combination with another oxygen atom (Eq. (6)) that has also been adsorbed (Eq. (5)) or by direct reaction with another N₂O molecule (Eq. (7)). It is possible that both the adsorption of N₂O (Eq. (3)) and desorption of O₂ (Eqs. (6) or (7)) are reversible, while all the other steps are irreversible.

The presence of SO₂ in the feed inhibited the N₂O decomposition reaction without actually changing the reaction mechanism, since no changes were measured with respect to the activation energy and the apparent activation order of N₂O. The only difference is that, in the presence of poisonous gases, O₂ indirectly affected
the reaction mechanism. We calculated zero reaction order in the presence of SO$_2$, while in the absence of SO$_2$ the reaction order was $-0.27$. In the former case oxygen is dissociatively adsorbed on the catalyst, thus, inhibiting the N$_2$O decomposition, but in the same time it is consumed according to the reaction:

$$\text{SO}_2 + \text{O} \rightarrow \text{SO}_3$$

SO$_3$ can react with the support to form surface sulphates [1] via the following reaction:

$$\text{Al}_2\text{O}_3 + 3\text{SO}_3 \rightarrow \text{Al}_2(\text{SO}_4)_3$$

4. Conclusions

Catalyst evaluation and reaction kinetic analysis was performed for the catalytic decomposition reaction of N$_2$O to N$_2$ in an O$_2$-rich atmosphere over Ru/Al$_2$O$_3$ in the absence and presence of SO$_2$ and H$_2$O gases that typically exist in flue gases and do not participate in the decomposition.

We loaded our Al$_2$O$_3$ support with Ru in the range of 1–4% and noticed that for Ru-loading higher than 2% the activity remained the same. We varied the procedure of the catalyst pretreatment using inert, reducing and oxidizing atmosphere before the introduction of the reactive gas mixture. In this way we modified the initial oxidation state of Ru. Experiments were carried out starting from the lowest or the highest reaction temperature. The same series of experiments were repeated adding SO$_2$ and H$_2$O in the feed. The highest activity was measured in the experiment that started at the highest reaction temperature when the catalyst was pretreated with He and the feed was SO$_2$ and H$_2$O-free.

The activity of Ru/Al$_2$O$_3$ was measured in the presence of SO$_2$ (0–500 ppm) and/or H$_2$O (0–10%) in the feed. A shift of the N$_2$O conversion versus temperature curve towards higher temperatures was observed when SO$_2$ and H$_2$O were added, either separately or simultaneously, to the feed. The inhibition caused by SO$_2$ was attributed to the formation of sulphates, while that caused by water to the competitive chemisorption of H$_2$O and N$_2$O on the same active sites.

Kinetic and TPD studies were carried out to examine the reaction mechanism that leads to the N$_2$ formation from N$_2$O under the reaction conditions of this work. Our results support a reaction path where N$_2$O is dissociatively adsorbed in the absence and presence of SO$_2$ and H$_2$O in the feed. The removal of oxygen from the catalytic surface is, probably, the controlling step for the N$_2$O decomposition.

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References