

A METHOD FOR THE DECOMPOSITION OF NITROUS OXIDE

FIELD OF THE INVENTION

The present invention relates generally to the catalytic decomposition of nitrous oxide (N_2O) into its elemental forms of O_2 and N_2 . More particularly, the present invention contemplates a catalytic process for decomposition of high concentration N_2O into its elemental forms in stack gas such as arising during adipic acid manufacturing or following other chemical processes. The catalyst utilized in accordance with the present invention is conveniently prepared from ruthenium (Ru) containing compounds (such as simple or complex ruthenium salts) and an alumina catalyst support. The catalysts $\text{Ru}/\text{Al}_2\text{O}_3$ advantageously show excellent catalytic performance and chemical/hydrothermal stability in a stack gas stream which contains N_2O , O_2 , CO_2 , CO and H_2O . The present invention advantageously provides, therefore, a cost-effective, catalytically efficient process for N_2O decomposition.

BACKGROUND OF THE INVENTION

In recent years, the development of clean technologies has gained increasing significance. In the area of air pollution control, the legislation concerning the exhaust emissions from automobiles as well as from many other chemical processes is being continuously strengthened. To meet this move, more active catalytic materials (catalysts) need to be developed. Furthermore, apart from catalytic activity considerations, improved catalyst performance and operation have to be achieved with a competitive cost structure for a particular application. In this regard, the development of new cost effective catalyst technology and its proper operation is an urgent task for pollutant emission control.

Nitrous oxide gas (N_2O) is a stratospheric ozone eliminator and a greenhouse gas responsible for global warming (Thiemens et al. Science 251 (1991) 932). In the nylon industry, N_2O is commonly produced as a gaseous by-product during the manufacture of adipic acid, a monomer used for nylon polymers. Due to the rise in the global production of nylon polymers, the magnitude of adipic acid industry N_2O emissions relative to those from other anthropogenic sources has been increased. In September 1991, major nylon polymer/adipic acid manufacturers worldwide had reached a general consensus that nitrous oxide in the adipic acid production off-gases should be substantially reduced by 1996-1998. Elimination of nylon source N_2O has become an urgent environmental issue for the nylon industry. With the tightening in legislation, emission levels of this gas are expected to become regulated within

a couple of years (Kapteijn et al. *Applied Catalysis B* 9 (1996) 24).

N₂O emissions in the adipic acid industry are currently controlled mainly by thermal methods which involve passing the off-gases through reducing flame boilers. Though these methods result in N₂O breaking down into its elemental forms N₂ and O₂, they are nevertheless, energy consuming. Catalytic decomposition techniques are offered as an alternative approach to reduce energy consumption in N₂O elimination as much lower temperatures can be used compared with those used in a simple thermal destruction method.

Nitrous oxide can be decomposed by a wide range of oxide catalysts (Kapteijn et al. *Applied Catalysis B* 9 (1996) 24), as reported for transition-metal (Ni, Cu, and Co) hydrotalcite-like (HT) catalyst precursors which have shown excellent catalytic activity (Swamy et al. US Patent No. 5,407,652 04/1995). As reported in the literature, metal oxide catalysts have been extensively investigated for N₂O decomposition, especially for low concentration applications (100-1000 ppm), such as in circulating fluidized beds for combustion and automotive exhaust emissions. Among the active catalysts reported so far, cobalt, copper, ruthenium, and rhodium based catalysts have shown excellent catalytic activity for N₂O decomposition. For example, using Cu/ZSM-5, a decomposition reaction rate of $2.7 \times 10^3 \mu\text{mol (N}_2\text{O)} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ has been obtained at 400°C. Rh/ZnO system has also been recently reported to be efficient in low-temperature N₂O (950 ppm) decomposition with the reaction of $4.0 \times 10^4 \mu\text{mol (N}_2\text{O)} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ at 300°C (Oi et al. *Chemistry Letters* 6 (1995) 453). However, this catalyst is deactivated significantly in a wet nitrous oxide stream. Recent advance in N₂O decomposition has indicated that ruthenium-exchanged zeolites, such as Ru-NaZSM-5 and Ru-HNaUSY, are able to decompose N₂O at relatively low-temperatures. Concerning the material cost, many of the above catalysts use precious metals, such as Pt, Pd, Ru, and Rh with a metal content of about 1-15 wt%, on various supports like alkali-earth metal oxides, zeolites and transition metal oxides (Li et al. US Patent No. 5,171,511 12/1992). For example Ru/Al₂O₃ catalyst with an Ru content of 1 wt% has been reported in literature with a N₂O decomposition activity of $1.9 \times 10^3 \mu\text{mol (N}_2\text{O)} / \text{g} \cdot \text{h}$ (GHSV = 30000 h⁻¹, N₂O = 990 ppm with He) at 400°C (Li et al. *Applied Catalysis B* 1 (1992) L21).

Although the above catalysts show significant activity for low concentration N₂O depletion, few studies reported in the open literature have been dedicated to the high concentration cases, such as that seen in the case of, for example, an off-gas stream of an adipic acid plant in which N₂O content normally ranges from 20 to 50 mol%. Furthermore, in this case nylon source N₂O gas in the off-gas stream is mixed with background gases such as O₂, CO₂, CO and H₂O. The effect of these gases on N₂O decomposition would thus be an important issue in the development of applicable catalysts for N₂O emission control in the adipic acid production industry. A useful catalyst would advantageously be able to withstand

non-ideal industrial process conditions (Zeng et al. Applied Catalysis B 13 (1997) 113).

According to the invention, a series of Ru oxide catalysts supported on alumina have been developed. The catalysts advantageously show excellent catalytic performance for high-concentration N_2O decomposition even with a low Ru content, for example of 0.2 wt%. A wide range of tests have been carried out, including an investigation of common background gases (H_2O , CO_2 , CO and O_2) in the specific example of off-gas streams of adipic acid plants in the nylon industry. In particular, the invention advantageously provides a process of decomposition of nitrous oxide using the above Ru-catalysts, and suitable activation/operation processes for the catalysts to work in a wet stack-stream environment. The invention also advantageously addresses general catalytic issues of activity evaluation, hydrothermal stability, reaction kinetics, aging test, space velocities, and catalyst characterization for water-containing high-concentration N_2O decomposition.

BRIEF SUMMARY OF THE INVENTION

The present invention describes a highly efficient and low-cost method for catalytic decomposition of nitrous oxide in nitrous oxide containing gases, for example in various exhaust streams of industrial or chemical processes.

According to the present invention there is provided a method for decomposing nitrous oxide in a nitrous oxide containing gas comprising: activating an alumina-supported ruthenium oxide catalyst in a gas stream or gas mixture in a fixed bed reactor, and introducing the nitrous oxide containing gas into the fixed bed reactor under conditions sufficient to convert the nitrous oxide to gaseous nitrogen and gaseous oxygen.

According to a preferred embodiment, the ruthenium metal in the catalyst has an oxidation state of less than or equal to +4 while the alumina support is in amorphous state or in gamma phase with sufficiently high specific surface areas.

Preferably the ruthenium component is present in the catalyst in the range of from 0.01 to 10 wt% based upon total weight of the catalyst. The heating temperature for catalyst preparation is preferably ranged between 25°C and 800°C using various heating schemes. The activation of catalyst may be conducted in a fixed bed reactor in various types of ambient gas at a temperature of from 200°C to 800°C and a pressure of from 0.1 to 300 atmospheres (atm). Typical gas hourly space velocity is in the range of 1000 h^{-1} to $300,000\text{ h}^{-1}$ during the activation.

It has been found that background gases such as those seen in for example, stack gases of adipic acid manufacturing plants give no significant deterioration to the nitrous oxide decomposition using the current catalytic approach. The catalysts are advantageously both

chemically and hydrothermally stable in a wet environment. According to this invention, decomposition of nitrous oxide is carried out in the same fixed bed reactor after the catalyst activation. The decomposition is preferably carried out at temperatures in the range of from 200°C to 800°C and at pressures of from 0.1 to 300 atmospheres. The gas hourly space velocity is preferably 1000 h⁻¹ to 300,000 h⁻¹ depending on the actual application.

A method of preparing an alumina-supported is also provided. The method comprises the steps of heating a ruthenium-loaded alumina support in temperature ramp modes or at one or more discrete temperature platforms ranging from about 25°C to 800°C for a period of 0.1 to 100 hours in a static gas or a flowing gas stream of a gas selected from noble gas, nitrogen, air and combinations thereof at pressures of from about 0.1 to 200 atmospheres.

The invention also provides a method for activating an alumina-supported ruthenium oxide catalyst comprising heating the catalyst in a fixed bed reactor at a temperature of from about 200°C to 800°C and at a pressure of from about 0.1 to 300 atmospheres.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the present invention will now be described in detail by way of example only with reference to the accompanying drawings in which:

Fig. 1 illustrates activation processes of wet catalyst with dry N₂O feed (30.1 mol% N₂O in He); Ru = 0.2 wt% catalyst 4.3 g (before moisturizing), feed rate = 83.3 ml/min, and GHSV = 1000 h⁻¹. Furnace temperature was fixed while the reaction was heading for steady state.

Fig. 2 illustrates effect of water addition on N₂O conversion (X); 4.3 g of Ru = 0.2 wt% catalyst, flow rate of the feed = 83.3 ml/min, and GHSV = 1000 h⁻¹. Feed compositions: (♦) 27.5 mol% N₂O in He; (Δ) 27.2 mol% N₂O and 1.1 mol% H₂O in He; (·) 26.9 mol% N₂O and 2.0 mol% H₂O in He; (◆) 26.7 mol% N₂O and 2.9 mol% H₂O in He.

Fig. 3 illustrates conversion (X) rate of N₂O in heating-cooling loops (4.3 g of Ru = 0.2 wt% catalyst, feed rate = 83.3 ml/min, and GHSV = 1000 h⁻¹) with various feeds: (a) 27.5 mol% N₂O in He; (b) 27.2 mol% N₂O and 1.1 mol% H₂O in He; (c) 26.9 mol% N₂O and 2.0 mol% H₂O in He; and (d) 26.7 mol% N₂O and 2.9 mol% H₂O in He.

Fig. 4 illustrates Arrhenius plots (based on data of Fig. 2) for N₂O decomposition reaction with feed compositions: (♦) 27.5 mol% N₂O in He; (Δ) 27.2 mol% N₂O and 1.1 mol% H₂O in He; (·) 26.9 mol% N₂O and 2.0 mol% H₂O in He; (■) 26.7 mol% N₂O and 2.9 mol% H₂O in He.

Fig. 5 illustrates effect of CO₂ on N₂O conversion (X) at 320, 360 and 400°C, using the Ru = 0.2 wt% catalyst (4.3 g); vol% = CO₂ flow rate / original N₂O in He flow rate (83.3

ml/min).

Fig. 6 illustrates O_2 effects on N_2O conversion (X) at 320, 360, and 400°C, using Ru = 0.2 wt% catalyst (4.3 g); $vol\% = O_2 \text{ flow rate} / \text{original } N_2O \text{ in He flow rate}$ (83.3 ml/min).

Fig. 7 illustrates N_2O conversion (X) as a function of operating time and feed composition at reactor temperatures of (a) 394.0°C and (b) 470.5°C; 4.3 g of Ru = 0.2 wt% catalyst, feed rate = 83.3 ml/min, and GHSV = 1000 h^{-1} .

Fig. 8 (a) illustrates N_2O conversion (X) versus flow rate and (b) activity of catalyst versus GHSV at various operating conditions: (♦) 30.9 mol% N_2O in He at 470.5°C, (■) 26.7 mol% N_2O and 2.9 mol% H_2O in He at 470.5°C, and (Δ) 30.9 mol% N_2O in He at 394.0°C; 2.16 g of the catalyst was used in all cases.

Fig. 9 illustrates the N_2O conversion (X) as a function of reaction temperature and Ru-content; 2.16 g of catalyst was used, flow rate of the feed = 601 ml/min, and GHSV = 14430 h^{-1} . Ru-content and feed compositions: (♦) Ru = 0.2 wt% and 30.4 mol% N_2O in He; (■) Ru = 1 wt% and 30.4 mol% N_2O in He; and (Δ) Ru = 2 wt% and 29.2 mol% N_2O in He.

DETAILED DESCRIPTION OF THE INVENTION

The process of the present invention utilizes Ru oxide catalysts which have preferably been prepared from ruthenium-containing salts or complexes and commercially available alumina supports which after appropriate heat-treatment / calcination and activation provide superior catalytic activity, chemical / hydrothermal stability and exceptional long-life under, for example, typical working conditions of adipic acid plants. Furthermore, a comprehensive range of testing has proved that this cost-effective catalyst system can also be operated in other nitrous oxide emitting chemical processes, such as in circulating fluidised beds for combustion and automotive emission control.

The catalysts may be formed by impregnating alumina pellet support with ruthenium-metal-containing solutions (Examples 1 and 2). The metal solutions preferably comprise, but are not limited to, ruthenium red ($Cl_6H_{42}N_{14}O_2Ru_3 \cdot 4H_2O$) solutions. The solutions may also be other inorganic/organic ruthenium-containing solutions. High ruthenium content catalysts are preferably prepared by an impregnation-then-evaporation method (Example 3). This may be conducted at temperatures of from 25°C to 150°C and a pressure at or below atmospheric pressure.

The heating treatment for the above ruthenium-loaded alumina can be conducted in various atmospheres such as common dry air, helium, nitrogen, oxygen, nitrous oxide, or combinations thereof at pressures of about 0.1 to 200 atmospheres (atm) for a period of 0.1

to 100 h to remove volatile decomposed products. The catalyst may be dried/heated during one or more periods utilizing one or more discrete temperature stages or using temperature ramping techniques known in the art. It is generally recommended that the drying, heating and calcination temperatures should not exceed 600°C to avoid unnecessary evaporation of ruthenium oxide species from the catalyst surfaces.

The amount of catalyst used may vary depending on the reaction conditions and the particular application for which the catalyst is to be used. The ruthenium content in the catalysts is preferably in the range of from about 0.01-10 wt%, more preferably about 0.1-1 wt%, even more preferably about 0.2 wt%. The preferred alumina supports have a specific surface area of 50-600 m²/g and are amorphous alumina or in the gamma crystallographic phase of alumina (γ -Al₂O₃). A preferred alumina support also possesses sufficient mechanical strength and toughness in fixed bed operation.

Following exposure of the catalysts to ambient air at low-temperatures, activation of the catalyst is preferably carried out at a reactor temperature of between 200-800°C. This advantageously reduces the transient period, namely the start-up process. The activation of the catalyst may be conducted directly in a dry or low-water-containing nitrous oxide stream to be decomposed before a steady-state operation. However, the temperature is preferably in the range of from 400-600°C to minimize Ru loss. Furthermore, it is envisaged that the activation step may also be carried out in a separate fixed bed reactor to that in which the nitrous oxide decomposition will take place. However, this is not preferred as cooling of the activated catalyst, or exposure to moisture may result in the need for reactivation prior to the decomposition process. It is preferred that the nitrous oxide decomposition be carried out at steady-state immediately after the above mentioned catalyst activation.

In this invention, the catalyst activation process may be selected from two options: (i) low activation temperature with long activation time, and (ii) high activation temperature with short activation time. The selection is dependent on actual application requirements.

The activation of the wet or new catalyst is conducted at a temperature which is slightly higher than the routine operation temperature. Although this generally shortens the transient period, the high-temperature operation also causes unnecessary deterioration of the catalyst. Therefore, deactivation factors of catalyst need to be balanced when a high processing temperature is selected.

The process may be used in a high-concentration N₂O containing stack gas stream, for example those which contain 10-100 mol% , more preferably 10-50 mol% of nitrous oxide. However, the process may also be utilized to remove nitrous oxide from essentially any gaseous stream containing N₂O, and is operative even when appreciable amounts of hydrocarbons, NO_x, water, oxygen, carbon dioxide, and carbon monoxide are present in the

N₂O containing gaseous mixture.

The operation temperature of the nitrous oxide decomposition process after the catalyst activation is preferably in the range of from 200-800°C, more preferably 300-600°C, but is not limited to these temperatures, to achieve a good balance of catalytic performance and energy saving. More particularly, the process can be advantageously run under fixed bed at pressures between about 0.1 to 300 atmospheres (atm) at a gas hourly space velocity (GHSV) ranging from 1,000 to 300,000 h⁻¹, preferably 1000-30,000 h⁻¹.

The stack gas of an adipic acid production plant may advantageously be treated for removal of N₂O when the stack gas temperature is within 300°C to 600°C. If, however, the stack gas temperature has been reduced significantly and the moisture (water) content of the stack gas exceeds 3 mol%, steps should be taken to reduce the excessive moisture to 3 mol% or lower before sending it to the decomposition reactor. Provided the moisture content of the process gases to be treated is below 5 mol% and preferably below 3 mol% the process gases may be treated for removal of N₂O according to the present invention down to room temperature. In addition to the consideration of water content and other background gases, optimal reaction conditions can be selected after balancing the cost of catalyst and operational energy consumption, namely reaction temperature.

The following examples are provided to further illustrate the detailed technical aspects of this invention and are not intended to limit the scope of the claimed invention.

GENERAL EXPERIMENTAL INFORMATION

The content of ruthenium on the calcined catalysts was determined by inductively coupled plasma (ICP) elemental analysis (Labtam Plasmascan F10). Specific surface areas of the catalysts were measured based on BET method (NOVA1000, Quantachrome). The catalysts were degassed at 350°C for 3 h at a base pressure 10⁻³ Torr before the nitrogen adsorption measurement at 77 K.

Crystallographic information of catalysts was established with the powder x-ray diffraction (XRD). The diffraction intensity - 2θ spectra were measured in a Philips PW 1729 with CuK_α radiation (λ = 1.5418 Å) at a scanning rate of 4° min⁻¹. Furthermore, metal-oxygen bonding situations of the catalysts were investigated with Fourier transform infrared spectroscopy (FTIR). Using KBr-pellet technique, the FTIR spectra of the catalysts were recorded with 4 cm⁻¹ resolution on a Shimadzu FTIR-8001. The catalyst to KBr ratio was optimized according to the general approach that the strongest bands should have intensities

in the transmission range 5-15%. One hundred scans were performed for each spectrum to obtain a good signal to noise ratio.

EXAMPLE 1

LOW Ru CONTENT CATALYST FABRICATION AND TREATMENTS

Ru = 0.2 wt% Ru/Al₂O₃ catalyst

50.0 g of the commercial catalyst support Al₂O₃ (pellets with $\phi = 3.2$ mm and $h = 3.4$ mm, SA = 105 m²/g, Alfa Products, Johnson Matthey) was immersed into a solution of ruthenium-red (Cl₆H₄₂N₁₄O₂Ru₃·4H₂O, Fluka Chemika) which was made from 2.25 g of Ru-red and 100.0 ml of deionized water. This static impregnation was carried out in a covered beaker at room temperature overnight (12 h). After impregnating, the catalyst was filtrated and then dried at 200°C for 2 h, followed by a calcination at 500°C for 4 h. All heating rates used in the drying and calcination routine were kept constant at 10°C/min. The thus prepared catalyst was stored in a dry box ready for use. To illustrate activation process of the catalysts, a small amount of the dry catalyst was moisturized in a humidifier with saturated water vapour at 25°C for 24 h; the resultant catalyst is called wet catalyst.

EXAMPLE 2

HIGH Ru CONTENT CATALYST FABRICATION AND TREATMENTS

Ru = 1 wt% Ru/Al₂O₃ catalyst

10.0 g of the commercial catalyst support Al₂O₃ (pellets with $\phi = 3.2$ mm and $h = 3.4$ mm, SA = 105 m²/g, Alfa Products, Johnson Matthey) was immersed into a solution of ruthenium-red (Cl₆H₄₂N₁₄O₂Ru₃·4H₂O, Fluka Chemika) which was made from 0.260 g of Ru-red and 30.0 ml of deionized water. The solution with Al₂O₃ pellets was stirred manually for 5 min at first, then left at room temperature for 1 h, followed by a soft stirring for another 5 min. Next, the solution and Al₂O₃ pellets were heated in an oven set at 80°C for 5 h with frequent stirring. Then, the temperature of oven was increased to around 105°C to remove the water from the solution phase, during which the solution and Al₂O₃ pellets were under a gentle and thorough stirring until no more solution phase. Finally, the ruthenium-red loaded Al₂O₃ pellets were calcined in air at 500 °C for 4 h. The heating rate was the same as that used in preparing 0.2 wt% Ru/Al₂O₃ catalyst, e.g. 10 °C/min.

Ru = 2 wt% Ru/Al₂O₃ catalyst

For 2 wt% Ru/Al₂O₃ catalyst, the preparation procedure was similar to the above 1 wt% case, except the concentration of Ru-red solution was changed. The solution in this case was made from 0.519 g of ruthenium-red (Cl₆H₄₂N₁₄O₂Ru₃·4H₂O, Fluka Chemika) and 30.0 ml of deionized water.

The general trend of BET measurement is that with increase of ruthenium content on the catalyst, specific surface area reduces rather linearly.

EXAMPLE 3

CATALYTIC DECOMPOSITION OF N₂O

Catalytic activity evaluation was carried out in a tubular quartz reactor ($\phi = 12$ mm) which was heated by a vertical electric tube-furnace (Carbolite). In a typical evaluative measurement, N₂O gas was continuously supplied from a gas cylinder (27.5-30.9 mol% N₂O, balanced with He) at a flow rate (F) of 83.3 ml/min using a Brooks 5950 mass-flow control system. The volume (V) of catalyst tested in the reactor was 5.0 ml (4.30 g), which corresponded a GHSV (F/V) of 1000 h⁻¹. Experiments with higher GHSV (up to 14430 h⁻¹) were also performed. The decomposed gases were cooled by passing a cooling coil and then vented through a scrubber. To determine N₂O conversion, inlet and outlet gas compositions were analyzed by gas chromatography method (Perkin Elmer Auto-System XL, TCD detector) using a Porapak Q column (4 feet in length, oven temperature 120°C) with He as the carrier gas (40 ml/min). To imitate stack gas of adipic acid plant, H₂O vapour was added to the feed by bubbling N₂O gas through a temperature controlled water evaporator, noting that the water content in the mixed feed depended on its saturated pressure at a specific temperature. To avoid any condensation of water vapour, the evaporator was operated at a temperature not higher than 25°C. Background gases, O₂, CO and CO₂, were introduced respectively from side cylinders to the N₂O gas line and then homogenized in a gas mixer. In these cases (O₂, CO, and CO₂), the flow rate of N₂O stream was kept constant at 83.3 ml/min, while the background gas was added to the feed gas in the measure of volume (i.e. mol) ratio to N₂O and He stream.

The catalytic activity was evaluated in terms of conversion rate (X) of the N₂O gas according to the following equation:

$$X = (P_{i,N_2O} - P_{f,N_2O}) / (P_{i,N_2O} + 0.5P_{i,N_2O}P_{f,N_2O}) \quad (1),$$

where P_{i,N_2O} and P_{f,N_2O} are partial pressures of N_2O of the initial and final gases respectively. It was noted that the partial pressures had the same values as their respective molar fractions since the experiment was conducted under normal pressure (1 atm). In view of the exothermic nature of N_2O decomposition, it is expected that reactor temperature will increase during the activation of catalyst (i.e. transient period; more and more N_2O being decomposed) when the furnace temperature is fixed. Each data point of X in Figs. 2 to 9 was measured after staying at a set temperature for 2.0-2.5 h to ensure both the reaction and thermal environment reached steady state.

EXAMPLE 4

ACTIVATION PROCESSES OF THE CATALYSTS

Using a dry N_2O stream, Fig. 1 shows two activation processes of the wet catalysts at fixed furnace temperature. In both cases, the reactor reached thermal equilibrium temperatures (394.0°C and 470.5°C respectively) after about 2 h of operation. However, over a period of 96 h, the high temperature activation increases the conversion from 75% to 99% and most of this increase is completed within 2 h. Although the low temperature activation process also indicates a 25% (from 6% to 31%) increment over the same period, the activation should be nevertheless described as a continuous process.

For the wet catalyst under a moisturized N_2O stream, the initial increases are less abrupt, compared to those in the dry N_2O stream (Fig. 1). Furthermore, unlike the previous two cases, more times (24 h) are needed to reach the thermal equilibrium temperatures (394.0°C and 470.5°C respectively). After 96 h of activation, the low temperature activation gives a conversion at 24.8% while the high temperature activation shows one at 97.6% (i.e. steady state with maximum conversion). It appears that the activation in a dry N_2O stream is more efficient than in a wet one.

For an operation at a temperature 20°C higher than 470.5°C, the thermal equilibrium (490.0°C) can be reached quickly within 2 h. Shorter times for thermal equilibrium and thus steady state reaction are needed in the operations at 510°C and 530°C which are 40°C and 60°C higher than 470.5°C respectively. It should be pointed out that the reactor temperature at 530°C is higher than the required, as 510°C has already given a near 100% conversion.

At high operation temperature, activity discrepancy between the dry and wet catalysts under the same experimental conditions is lessened, which indicates that there is no permanent

deactivation in the catalyst when it is wet-treated.

EXAMPLE 5

N₂O DECOMPOSITION WITH WATER

It has been shown in the previous section that the activation of catalyst in a wet stream is less efficient than in a dry one. Fig. 2 describes a general behaviour of the activated catalyst working in different wet streams. From these conversion-versus-temperature curves, it is found that the effect of added water on the conversion varies with reaction temperature. For example, the gap among the curves is widened over the temperature range of 350-450°C, especially at the temperatures around 400°C, which corresponds to 40-60% conversions.

The water effect is non-linear over these temperatures. The gap between 1 mol% and 2 mol% of water is bigger than those between 0 mol% and 1 mol% and between 2 mol% and 3 mol%, although the concentration of water in the feed streams is increased linearly.

EXAMPLE 6

HYDROTHERMAL STABILITY OF THE CATALYSTS

As demonstrated in Fig. 3, the heating-cooling curves are perfectly overlapped no matter whether water is added or not. Second, all these curves are identical to their respective counterparts (i.e., with the same composition of feed) in Fig. 2.

The reversibility indicates that once the catalyst has been activated at an elevated temperature, N₂O can be decomposed in co-presence of water and no dehydration of the gas is needed in a practical off-gas treatment. Water reacts chemically with neither the catalyst nor the N₂O at these reaction temperatures.

EXAMPLE 7

KINETICS OF WET DECOMPOSITION

Decomposition reaction of nitrous oxide using the current claimed process can be described by the following reaction kinetics:

$$-dP_{N_2O}/dt = kP_{N_2O} \quad (2).$$

The integration of Eq. (2) gives:

$$\ln\{\ln(P_{i,N_2O}/P_{f,N_2O})\} = \ln A - \ln(F/V) - E_a/RT \quad (3).$$

where V is the volume of the catalyst bed, F is gas flow rate, A is Arrhenius pre-exponential factor, and E_a is apparent activation energy of the decomposition. Plotting $\ln\{\ln(P_{i,N_2O}/P_{f,N_2O})\}$ against $1/T$ in Fig. 4 for the cases in Fig. 2, it is found that all data can be fitted nicely into straight lines. No marked difference in slope can be identified among the four fits. The apparent activation energies calculated are 139, 143, 140 and 133 kJ/mol respectively for the four cases in sequence of water content (averaged $E_a = 139$ kJ/mol). It is therefore concluded that the decomposition kinetics of N_2O in wet atmosphere is essentially similar to that in the dry one with N_2O adsorption as rate-limiting step.

EXAMPLE 8

N_2O DECOMPOSITION WITH CARBON DIOXIDE

For the current catalyst system, results of $N_2O + CO_2$ decomposition are shown in Fig. 5. Since constant conversion rates are clearly maintained for all the temperature studied, it is believed that the catalyst surface is chemically inert towards CO_2 . The chemical adsorption of CO_2 on the catalyst surface is rather difficult, since a competitive adsorption of CO_2 would certainly reduce the active sites for N_2O , causing a drop in the conversion.

EXAMPLE 9

N_2O DECOMPOSITION WITH OXYGEN

According to the existing decomposition models in the literature, the decomposed product oxygen has been often related to reaction rate in the form of $(P_{O_2})^{-(0.5-1.0)}$. This gas also shows a small effect on the decomposition rate in the current catalyst system. As indicated in Fig. 6, the effect, however, is only significant in low temperature reaction ($320^\circ C$). For higher decomposition temperatures (360 and $400^\circ C$), this effect is almost negligible, though it still shows a decline trend.

EXAMPLE 10

LIFE TESTING OF THE CATALYSTS

For the mid-range temperature ($394.0^\circ C$; around 30-50% conversion), the difference in

conversion due to the presence of water is substantial. As shown in Fig. 7, a 20% lowering of conversion is observed in 3% H₂O stream (bottom line, Fig. 7a), compared to that of dry stream (top line, Fig. 7a). The gap has been significantly reduced for high temperature operation. In fact, less than 2% changes between the dry and wet streams are found for the operation temperature at 470.5°C (Fig. 7b). In all cases the activity of the catalysts is remarkably stable over a non-stop continuous process of 48 h, giving no sign of deterioration regardless the content of water and operation temperature. The catalyst had been operated throughout a total heating period of 1680 h, and no observable deactivation had been found.

For the used catalyst (after 1680 h), a slight decrease in surface area from 89 m²/g to 76 m²/g is observed. The reduction in surface area can be attributed to the grain growth proposed earlier due to the prolonged heating. FTIR spectra measured for the as-prepared, used, and wet catalysts are similar, showing typical Al₂O₃ characteristics. Furthermore XRD spectra indicate the γ -Al₂O₃ phase (JCPDS file no. 10-0425) is predominant in these catalysts, noting that Ru-metal/catalyst = 0.20 wt%. Spectral characteristics of RuO₂ and hence possible RuO_{2-x} phase (JCPDS file no. 40-1290) can also be observed. The intensities of the XRD peaks are basically unaltered, confirming there was no major metal (Ru) loss or structural variation of the Ru/ γ -Al₂O₃ catalysts before and after different kinds of hydrothermal treatments. This materials characterization confirms that the catalysts of this invention are both chemically and hydrothermally stable and can withstand extreme conditions imposed by the industrial requirement.

EXAMPLE 11

DECOMPOSITION AT HIGHER GAS FEED RATES

A significant increase in conversion rate can be achieved by increasing the space velocity. As revealed in Fig. 8, an increase of 7.2 times in flow rate (and thus GHSV) results in only about 30% of conversion drop using a wet N₂O steam and less than 30% drop using a dry stream. Therefore, fast feeding can be very beneficial for N₂O decomposition. For the moderate temperature operation (such as at 394.0°C), the conversion is almost unaltered with rapid increase in GHSV. A linear relationship between the activity and GHSV can be obtained respectively for the three series of experiments and excellent catalytic performance has been evidenced. With the Ru = 0.2% catalyst, activities of 1.4×10^2 mmol (N₂O)/g·h (GHSV = 14430 h⁻¹, N₂O = 30.9 mol%, balanced with He) and 1.2×10^2 mmol (N₂O)/g·h (GHSV =

14430 h⁻¹, N₂O = 29.9 mol%, H₂O = 3.0 mol%, balanced with He) are attainable for the dry and wet conditions respectively at 470.5°C. Only an averaged drop of 15% in activity is found using the wet N₂O feed. The above evaluated activity in wet stream is comparable to that reported for a Co-HT catalyst (Co/Al = 2.2) operated at 475°C (GHSV = 18000 h⁻¹, N₂O = 15 mol%, H₂O = 2 mol%, balanced with He; Swamy et al. US Patent No. 5,407,652 04/1995). In Fig. 8, the activity for the low temperature dry-operation is about half of that of the high temperature one, when temperature is lowered from 470.5°C to 394.0°C.

EXAMPLE 12

DECOMPOSITION WITH HIGH Ru CONTENT CATALYSTS

Fig. 9 illustrates the N₂O conversion using higher Ru-content catalysts. As can be seen, the excellent catalytic activity is obtained. For example, the activity of 1 wt% Ru/Al₂O₃ catalyst is 1.63×10^2 mmol (N₂O)/g·h and that of 2 wt% Ru/Al₂O₃ catalyst is 1.65×10^2 mmol (N₂O)/g·h at 400°C [Feed rate = 601 ml/min (GHSV = 14430 h⁻¹) and weight of catalyst = 2.16 g]. These catalysts are about 80 times more active than reported for a 1 wt% Ru/Al₂O₃ catalyst prepared by other method at the same reaction temperature (Li et al. Applied Catalysis B 1 (1992) L21). In fact our 0.2 wt% Ru/Al₂O₃ catalyst [activity = 62 mmol (N₂O)/g·h at 400°C with feed rate = 601 ml/min (GHSV = 14430 h⁻¹) and weight of catalyst = 2.16 g] is already about 30 times more active than the above-mentioned 1 wt% Ru/Al₂O₃ catalyst.

In Fig. 9, an increase of ruthenium content from Ru = 0.2 wt% to 1 wt% (about 5-times) results in a doubling of conversion rate (*X*) at 400°C. Therefore the activity of Ru = 0.2 wt% catalyst is superior in terms of cost-effectiveness when considering better utilization of ruthenium metal at higher reaction temperatures.

PRESENTATION OF DATA

The conversion data (*X*) in this invention have been presented graphically in Figs. 1-9. In addition to these graphical data, Table 1 presents the preparation parameters for making low Ru-content catalysts (Ru = 0.07-0.26 wt%) according to the procedure of Example 1. The results demonstrates that the Ru-content on the surface of alumina can be tailor-made according to the concentration of Ru in the solutions.

TABLE 1.

Catalyst Ru wt%	Ru-red dissolved Ru-red(g)/H ₂ O(ml)	Ru-red concentration g/ml	Thermal-treatment °C(h)
0.07	0.0883/20.0	4.4×10^{-4}	200(2)/500(4)
0.11	0.1766/20.0	8.8×10^{-3}	200(2)/500(4)
0.15	0.2650/20.0	1.3×10^{-2}	200(2)/500(4)
0.18	0.3500/20.0	1.8×10^{-2}	200(2)/500(4)
0.19	0.4000/20.0	2.0×10^{-2}	200(2)/500(4)
0.20	0.4500/20.0	2.3×10^{-2}	200(2)/500(4)
0.21	0.5000/20.0	2.5×10^{-2}	200(2)/500(4)
0.24	0.7500/20.0	3.8×10^{-2}	200(2)/500(4)
0.26	1.0000/20.0	5.0×10^{-2}	200(2)/500(4)

Notes: (i) For each batch catalyst, 10.0 g of as-received Al₂O₃ support was soaked in 20.0 ml Ru-containing solution indicated above; and (ii) Ru-loading (wt%) on Al₂O₃ support was determined by ICP method.

Table 2 presents the conversion data when carbon monoxide is added to the nitrous stream. The data demonstrate again that the present claimed process is very efficient in converting nitrous oxide. In fact, the CO addition enhances the catalytic performance.

TABLE 2.

CO in Feed mol%	N ₂ O Conversion at 394°C	N ₂ O Conversion at 471°C
0	55.2	99.2
0.2	57.2	99.3
0.9	60.8	99.3

Notes: (i) Catalyst: Ru = 0.2 wt%, 4.3 g.

(ii) N₂O initial concentration 27.9 mol%, balanced with He.

(iii) Flow-rate of N₂O (27.9 mol%) = 83.3 ml/min was fixed, while CO was added to the stream.

Table 3 provides a comparison of the catalytic activity of the catalysts based on the claimed process (after activation of catalyst). These selected data demonstrate that the present invention provides exceptionally excellent catalytic performance in tuning nitrous oxide into its

elemental forms, namely oxygen and nitrogen. They are remarkably active compared to the most active catalysts known in the open literature/patents at the similar reaction temperatures and GHSV range.

TABLE 3

Catalyst/weight Ru wt% / g	Flow-rate/GHSV ml/min / h ⁻¹	Feed Composition* mol%	Temperature °C	Activity mmol (N ₂ O)/g·h
0.2 / 2.16	601 / 14430	N ₂ O: 30.9	394	67.0
0.2 / 2.16	601 / 14430	N ₂ O: 30.9	471	141.0
0.2 / 2.16	601 / 14430	N ₂ O: 29.9 & H ₂ O: 3.0	471	117.0
0.2 / 2.16	601 / 14430	N ₂ O: 30.4	400	62.3
1.0 / 2.16	601 / 14430	N ₂ O: 30.4	400	162.3
2.0 / 2.16	601 / 14430	N ₂ O: 29.2	400	164.5

Note: * Balanced with helium.



CLAIMS

1. A method for decomposing nitrous oxide in a nitrous oxide containing gas comprising: activating an alumina-supported ruthenium oxide catalyst in a gas stream or gas mixture in a fixed bed reactor, and introducing the nitrous oxide containing gas into the fixed bed reactor under conditions sufficient to convert the nitrous oxide to gaseous nitrogen and gaseous oxygen.
2. The method according to claim 1 wherein the catalyst has a ruthenium content of from 0.01 to 10 wt%.
3. The method according to claim 2 wherein the catalyst has a ruthenium content of about 0.2 wt%.
4. The method according to claim 1 wherein the alumina catalyst support is gamma alumina or amorphous alumina which has a specific surface area of 50 m²/g to 600 m²/g.
5. The method according to claim 1 wherein the ruthenium is introduced to the alumina support by an impregnation or impregnation-then-evaporation technique at temperatures of from 25°C to 150°C and a pressure at or below atmospheric pressure.
6. The method according to claim 5 wherein the ruthenium is introduced to the support as an inorganic or organic solution of at least one ruthenium-containing compound.
7. The method according to claim 6 wherein the ruthenium is introduced to the alumina support as an aqueous solution of ruthenium-red (Cl₆H₄₂N₁₄O₂Ru₃·4H₂O).
8. The method according to claim 1 wherein the alumina-supported ruthenium oxide catalyst is formed by heating a ruthenium-loaded alumina support in temperature ramp modes or at one or more discrete temperature platforms ranging from 25°C to 800°C for 0.1 to 100 hours in a static gas or flowing gas stream of a gas selected from noble gas, nitrogen, air and combinations thereof at pressures of from 0.1 to 200 atmospheres (atm).
9. The method according to claim 1 wherein the ruthenium has an oxidation state of +4 or less.
10. The method according to claim 1 wherein the catalyst is activated under a gas stream or gas mixture of a gas selected from noble gas, nitrogen, carbon monoxide, oxygen, nitrous oxide and combinations thereof.
11. The method according to claim 10 wherein the catalyst is activated in-situ under a dry or wet nitrous oxide gas stream at a temperature higher than, equal to or lower than the operational temperature of the nitrous oxide decomposition.
12. The method according to claim 10 wherein the catalyst is activated in a stack gas stream of an adipic acid plant at a temperature higher than, equal to or lower than the





operational temperature of the nitrous oxide decomposition.

13. The method according to claim 10 wherein the activation of the catalyst is conducted in the fixed bed reactor at a temperature of from 200°C to 800°C and a pressure of from 0.1 to 300 atmospheres.

14. The method according to claim 1 wherein the activation of the catalyst is conducted in a gas stream having a gas hourly space velocity ranging from 1,000 h⁻¹ to 300,000 h⁻¹.

15. The method according to claim 15 wherein the nitrous oxide containing gas contains at least one background gas.

16. The method according to claim 17 wherein the at least one background gas is water vapour, oxygen, carbon monoxide, carbon dioxide, noble gas, or mixtures thereof.

17. The method according to claim 1 wherein the nitrous oxide concentration in the nitrous oxide containing gas is in the range of from 0.001 to 100 mol%.

18. The method according to claim 1 wherein the nitrous oxide concentration in the nitrous oxide containing gas is in the range of from 10 to 100 mol%.

19. The method according to claim 18 wherein the nitrous oxide concentration in the nitrous oxide containing gas is in the range of from 30 to 50 mol%.

20. The method according to claim 1 wherein the water content of the nitrous oxide containing gas is reduced through condensation by cooling the gas mixture down to room temperature before sending it to the fixed bed reactor.

21. The method according to claim 1 wherein the nitrous oxide decomposition is conducted at a temperature of from 200°C to 800°C and a pressure of from 0.1 to 300 atmospheres.

22. The method according to claim 18 wherein the nitrous oxide decomposition is carried out at a gas hourly space velocity of from 1,000 h⁻¹ to 300,000 h⁻¹.

This Sheet Has Been Replaced

