



Modified KIT-6 and SBA-15-spherical supported metal catalysts for N₂O decomposition

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ABSTRACT

Nitric acid and adipic acid plants are the main producers of nitrous oxide (N₂O), a greenhouse gas that damages the ozone layer and causes environmental issues. In the present work, an attempt has been made to modify KIT-6 and SBA-15-spherical mesoporous silica to enhance the hydrothermal stability and increase the acidic sites on the surfaces through post salt addition and aluminum (Al) incorporation, respectively, in order to effectively utilize them as supports for different metals (Rh, Ru, Pd, Fe) supported catalysts for N₂O decomposition. Each metal loadings of 1 wt.% was impregnated onto the modified mesoporous silica support materials. The materials were characterized by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), ammonia temperature programmed desorption (NH₃-TPD), nitrogen adsorption/desorption, X-ray diffraction (XRD) and transmission electron microscope (TEM) analysis techniques. The potential of these modified mesoporous silica supported Rh, Ru, Pd or Fe (1 wt.%) powder catalysts has been examined in a small laboratory scale reactor under specific N₂O decomposition conditions. The order of activity of the metals on the modified mesoporous silica supports was: Rh > Ru > Pd > Fe. The modified mesoporous silica supported Rh, Ru and Fe catalysts showed an enhanced activity for N₂O decomposition, compared to the non-modified mesoporous silica supported catalysts, due to an increase in the intermediate acidic sites on the supports. However, a different effect was found for the modified mesoporous silica supported Pd catalysts. The hydrothermal stability of the optimized mesoporous silica supported Rh catalysts indicates that these catalysts could be promising candidates for N₂O decomposition application.

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Introduction

Nitrous oxide (N₂O) has been identified as a potential contributor to ozone layer depletion in the stratosphere and as a relatively strong greenhouse gas [1,2]. The global warming potential of N₂O is 310 and 21 times greater than that of CO₂ and CH₄, respectively [1–4]. The ambient level of N₂O is 314 ppb, and has constantly increased in recent years [2]. N₂O is produced by both natural and anthropogenic sources. The primary natural sources of N₂O are the biological processes that take place in soils and oceans. Fertilizers, nitric acid, adipic acid, caprolactam and glyoxal production, fossil fuels and biomass combustion, as well as sewage treatment are the main contributors of the anthropogenic sources [5–7]. However, the main anthropogenic sources are nitric and adipic acid plants [5,8]. Nitric acid is increasingly used for fertilizer production and it is manufactured through oxidation of ammonia [2]. During this catalytic oxidation process, N₂O is

produced as a byproduct. Therefore, a reduction in N₂O emissions is currently a target. Catalytic N₂O decomposition is considered to be the most effective and economical way of achieving this goal [9].

Noble metals, metal oxides, mixed oxides, perovskite-type oxides, and metal or ion exchanged zeolites are known to be active for N₂O decomposition at higher temperature [10–17]. Rhodium or iridium oxides have been found to be more active for N₂O decomposition than other oxides; however, their low surface areas contribute to their main disadvantages [6]. The metal supported catalyst is another interesting alternative. Zeolites are the most widely used supports and have been studied for use in metal supported catalysts for this application. However, the low exchange capacity of the metals in zeolite, due to their microporosity and low surface area, limits its use, and an alternative support with a high surface area would be more attractive and necessary for this application [10]. Mesoporous silicas with high surface areas, pore volumes and a narrow pore size distribution are very interesting alternatives to conventional zeolites and alumina materials [6]. Mesoporous silica supported catalysts have recently been applied for N₂O degradation and have shown comparatively better activity, as can be seen in the

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literature [6,9,10]. These mesoporous silicas can be used as interesting catalyst supports for metal oxides and metals due to the combination of good accessibility, uniform pore size and high surface area. However, they also suffer from poor hydrothermal stability and low acidic sites on the surface.

SBA-15-Spherical shaped (SBA-15-S) with a much larger 2-dimensional pore size and uniform shape was used for the first time for N_2O decomposition in a recent work of ours [6] and it showed a better access and accessibility of metals and a better transportation of reactants and products. Similarly, the Korea Advanced Institute of Science and Technology (KIT-6) silica with a 3-dimensional (large-pore gyroid cubic Ia3d) pore structure, which has recently received the attention of many researchers for various applications [18–20], was also tested in a previous work for N_2O abatement [6]. However, these mesoporous material supported Rh catalysts were not very stable for long periods and showed deactivation after a certain time span.

Therefore, in the present work, we have further developed these SBA-15-S and KIT-6 supported Rh catalysts in order to obtain a more effective application of N_2O decomposition. Post salt addition has been used to improve the hydrothermal stability [21] of the SBA-15-S and KIT-6 support materials in order to remove the low hydrothermal behaviour of these materials. The role of acidity in N_2O decomposition catalyst has also been subject to debate [22]. Therefore, moderate acidic sites were created by incorporating aluminum (Al) on the surface of the SBA-15-S and KIT-6 supports. Rh, Ru, Pd and Fe were chosen to obtain the optimized metals with the highest activity for these modified support materials. The materials were characterized by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), ammonia temperature programmed desorption (NH_3 -TPD), nitrogen adsorption/desorption, X-ray diffraction (XRD) and transmission electron microscope (TEM) analysis techniques to establish their characteristics. The modified KIT-6 or SBA-15-S supported metal powder catalysts have been compared with the non-modified mesoporous silica supported metal powder catalysts. Stability tests of the optimized modified material supported metal catalysts have also been performed.

Experimental

Materials

The following reagents were used for the synthesis and modification of the SBA-15-S and KIT-6 support materials and for the formation of the supported metal catalysts, without any further purification: Pluronic P123 (P123, Aldrich), hydrochloric acid (HCl, 37%, Sigma–Aldrich), tetraethyl orthosilicate (TEOS, 98%, Aldrich), potassium chloride (KCl, 99%, Sigma Aldrich), mesitylene (Aldrich), 1-butanol (99.5%, Fluka), sodium chloride (NaCl, 99%, Fluka), ethylenediamine tetraacetic acid tetrasodium salt (EDTANa₄, pure, Junsei), aluminum chloride (AlCl₃, Sigma Aldrich), ethanol (99.8%, Fluka), rhodium(III) nitrate solution (10 wt.% Rh in >5 wt.% nitric acid, Aldrich), Ruthenium(III) nitrosyl nitrate solution (1.5 wt.% in dilute nitric acid, Aldrich), palladium(II) nitrate solution (10 wt.% Pd in >10 wt.% nitric acid, 99.999%, Aldrich) and iron(III) nitrate nonahydrate (ACS reagent, >98%, Sigma–Aldrich).

Synthesis of the mesoporous silica supports and their modification by post salt addition and Al incorporation

The siliceous SBA-15-S and KIT-6 materials were synthesized according to the procedures reported in our previous work [6]. After synthesis, the materials were dried and eventually post salt treated according to the procedure reported in [21] using NaCl.

Few drops of EDTANa₄ were used to adjust the pH of the solution equal to 10. After 12 days, the precipitate was filtered and washed with hot distilled water before cooling. Samples were dried at 100 °C, washed with an ethanol-HCl mixture, and calcined in air in static conditions at 550 °C for 5 h.

The Al-SBA-15-S and Al-KIT-6 (Si/Al = 5, 20) materials were prepared by means of the post-aluminum incorporation technique [21]. The siliceous or post salt treated SBA-15-S and KIT-6 materials were heated in a drying oven at 100 °C for 10 h to remove water. AlCl₃ in ethanol was added to the materials in polypropylene bottles and stirred vigorously for 30 min. The mixtures were filtered, washed with ethanol and dried at 110 °C in an oven. Dried materials were also washed with 1 M HCl to remove extra-framework aluminum and finally calcined in air at 550 °C for 5 h.

Mesoporous silica supported metal catalyst formation and characterization

Modified or non-modified SBA-15-S and KIT-6 supported Rh or Ru or Pd or Fe (1 wt.%) catalysts were synthesized by means of the incipient wetness method, using nitrate precursors. After impregnation, each catalyst was dried in an oven at 100 °C for 12 h. The catalysts were then calcined at 550 °C for 6 h in the presence of air to obtain the supported rhodium oxide catalysts.

SEM FEI Quanta Inspect 200 was used to observe the morphology of the modified mesoporous silicas. EDAX Genesis, with an SUTW detector equipped with SEM equipment, was used to carry out the EDX analysis in order to confirm the presence of silica and Al.

The acidic property of the siliceous and the modified mesoporous silica support samples was analyzed by means of NH_3 -TPD using a TPD/R/O 1100 analyzer, equipped with a thermal conductivity detector (TCD). A fixed catalyst bed was enclosed in a quartz tube and sandwiched between two quartz layers, following pretreatment in a helium flow, heated to 500 °C with 10 °C/min, and kept at 500 °C for 2 h. The samples were cooled to 100 °C and ammonia was injected. After physisorption of the ammonia, the catalyst was purged with helium. A TPD test was carried out up to 550 °C, at a 5 °C/min flow rate under helium. The desorbed NH_3 was detected in the outlet flow using the TCD detector.

The Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}), pore volume (PV) and average pore diameter (APD) were measured on the powder materials, which had previously been outgassed at 150 °C using Micromeritics FlowPrep 060, USA (sample degas system), by means of N_2 sorption at 77 K on a Micromeritics Tristar II, USA (surface area and porosity) instrument.

Small-angle X-ray diffraction (XRD) patterns of the materials were recorded on an X'Pert Phillips diffractometer using Cu K α radiation at $2\theta = 0.1$ – 5° . Moreover, high-angle XRD patterns of the optimized mesoporous silica supported Rh catalysts were obtained at $2\theta = 5$ – 60° .

TEM images were collected from the thin edges of the sample particles with a JEOL TEM 2010 (JEOL Ltd.) electron microscope, operating at 200 kV.

N_2O abatement reaction

The activity of the prepared catalysts was analyzed by means of temperature programmed reaction (TPRe), according to a standard operating procedure: a gas mixture (1700 ppm N_2O , He = balance) was fed at a constant rate of 100 mL/min, via a set of mass flow controllers, to the catalytic fixed-bed micro reactor, which was enclosed in a quartz tube placed in an electric oven. The tubular quartz reactor was loaded with 50 mg of catalyst pellets (250–425 μ m). The W/F of the gases through the catalytic bed was

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