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Ruthenium(III) ion-exchanged zeolite Y as highly active and reusable catalyst in decomposition of nitrous oxide to sole nitrogen and oxygen

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ABSTRACT

Ruthenium(III) ion-exchanged zeolite Y, prepared by ion exchange of Ru^{+3} ions with the extra framework Na^+ cations in zeolite Y with a Si/Al ratio of 2.5, is employed to catalyze the decomposition of nitrous oxide to nitrogen and oxygen. Catalytic activity of ruthenium(III) ion-exchanged zeolite Y is studied in the decomposition of nitrous oxide to nitrogen and oxygen depending on the ruthenium loading of zeolite and flow rate of nitrous oxide helium mixture in a continuous flow vertical reactor. The results collected reveal that ruthenium(III) ion-exchange zeolite with a ruthenium loading of 3.98 wt.% is highly active, long-lived, and reusable catalyst providing 100% conversion of nitrous oxide to sole nitrogen and oxygen at 350 °C without any side reaction. This catalyst can be bottled under ambient conditions and repeatedly used in successive runs of nitrous oxide decomposition for up to 5 months without significant loss in activity. Intrazeolite ruthenium(0) nanoclusters are slightly less active than the ruthenium(III) ion-exchanged zeolite Y in decomposition of nitrous oxide, which might be attributed to the migration of ruthenium(0) to the external surface before oxidation at high temperature. The other two metals of Group 8, iron(III) and osmium(III) ion-exchanged zeolite Y do not show activity as high as that of ruthenium(III) ion-exchanged zeolite Y in the same reaction.

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1. Introduction

Nitrous oxide (N_2O) has recently received growing interest because of its increasing contribution to the global warming [1] and ozone layer depletion [2]. As a greenhouse gas, nitrous oxide has a global warming potential (GWP) as much as 310 and contributes to the global warming by 6% of the total [3]. The foremost concern is on the increasing rate of N_2O concentration in the atmosphere (0.2–0.3% per year) mainly due to the anthropogenic activities [4,5]. Regarding its potential threat on the global environment, attentions have recently been drawn to seek for the efficient technologies for the abatement of nitrous oxide [6]. The catalytic decomposition of nitrous oxide to sole nitrogen and oxygen has been suggested as the most economical process [7]. This suggestion has been well accepted as the process converts a potentially hazardous gas solely to two harmless atmospheric gases.

$$N_2O(g) \rightarrow N_2(g) + \frac{1}{2}O_2(g) + \text{Heat} \quad (1)$$

On the other hand, nitrous oxide is also a valuable chemical in defense industry since it can be used as both fuel and oxidizer in liquid propellant rocket engines and hybrid systems [8,9]. Nitrous oxide is nontoxic and stable at ambient temperature and compatible with common structural materials [10]. Moreover, the exothermic decomposition of N_2O (Eq. (1)) gives the opportunity of obtaining high temperature air for the air supply systems of high speed air breathing engine all-up round tests. Decomposition of nitrous oxide results in production of free oxygen which can be used as oxidizer for a wide variety of fuels [11]. Although the exothermic decomposition of nitrous oxide (Eq. (1)) generates 82 kJ $mol^{-1}$of heat [12], the energy barrier of decomposition is quite high (250 kJ mol^{-1} [13]. That is why the reaction can occur at appreciable rates only at high temperature. In the classical manner, gas is heated to above 1000 °C in order to attain the required reaction rates. However, working with such high temperatures is not feasible and almost impossible for large scale systems. On

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the other hand, the energy barrier of the reaction and thus the reaction temperature can be drastically lowered by using a suitable catalyst.

Widely used catalysts in decomposition of nitrous oxide are the transition metals supported on oxides [14] or ion exchanged into zeolites [15–18]. The transition metal ions, iron(III), cobalt(II), copper(II), ruthenium(III) and rhodium(III), ion-exchanged into ZSM-5 or BEA have been tested as catalyst in decomposition of nitrous oxide [19–21] and the latter two have shown to be the most active ones, providing complete conversion of nitrous oxide to nitrogen and oxygen at 350 °C by using 0.6% metal loading of zeolite [21]. However, in that study, the durability and reusability of catalysts have not been tested and the effect of metal loading on the catalytic activity has not been reported either. Mc Carty et al. have used US-Y with a relatively high silica–alumina ratio (Si/Al = 29) as support and ruthenium(III) ion exchanged US-Y with different metal loading as catalyst in decomposition of nitrous oxide [22,23]. Although they have shown high activity of the catalyst in decomposition of nitrous oxide at temperature as low as 200 °C, the durability and reusability of the catalyst have not been reported as acid zeolites cannot be stored and used at ambient conditions since they can easily decompose with humidity. Ruthenium(III) ion exchanged Beta, zeolite Y and ZSM-5 prepared by using the $[Ru(NH_3)_6]^{3+}$ complex ion have been tested as catalyst in decomposition of nitrous oxide and only 70% conversion could have been achieved at 450 °C as measured by gas chromatography [24]. $[Ru(NH_3)_6]^{3+}$ may not be an appropriate cation to be ion-exchanged into zeolite Y since its diameter is very large to get into the pores of zeolite Y at room temperature. That may be the reason of not obtaining a complete conversion at 450 °C. Labhsetwar et al. have synthesized Ru+Ag/US-Y and Ru+Co/US-Y catalysts by applying two step ion-exchange reaction [25]. In the first step, $RuCl_3$ has been ion-exchanged into US-Y, while $AgNO_3$ or cobalt acetate solutions were used for the second ion-exchange into Ru-Us-Y. However, complete decomposition of nitrous oxide could have been achieved at ~450 °C for Ru+Ag/US-Y, while Ru+Co/US-Y could provide complete decomposition of nitrous oxide at ~350 °C.

Although some efforts have been devoted to use the transition metal ion-exchanged zeolite Y on decomposition of nitrous oxide, a thorough investigation of these catalytic materials have not been reported yet. The catalytic properties such as durability, reusability, activity depending on the metal loading of zeolite need to be studied. Also the selection of metal ion to be used in ion-exchange is important as well as the zeolite in obtaining the metal ion-exchanged zeolite with the desired amount of metal ions within cages of zeolite. The metal ions remained on the external surface of zeolite are not as active as the ones in the cages. As observed in some of previous studies [24], an incomplete ion-exchange of metal ions into zeolite may cause to a lower conversion rate or high temperature required for an appreciable rate of conversion.

Herein we report the use of ruthenium(III) ion-exchanged zeolite Y as catalyst in decomposition of nitrous oxide. Zeolite Y with a silica/alumina ratio of Si/Al = 2.5 was selected as a suitable host material as it is stable in aqueous solution as well as solid at high temperatures up to 600 °C. Ion exchange of ruthenium(III) into zeolite Y is achieved by using $RuCl_3{\cdot}3H_2O$ which is soluble in water. Aqueous ruthenium(III) ion is small enough to enter the cages of zeolite Y through the 7.4 Å aperture [26]. Ruthenium(III) ion-exchanged zeolite was tested as catalyst in decomposition of nitrous oxide and found to be highly active catalyst providing 100% conversion at 350 °C. For comparison, the other two metals, iron and osmium of the Group 8, which were also ion-exchanged into the zeolite from metal(III) chloride solution, were also tested in the same decomposition reaction. Our report also includes the test of intrazeolite ruthenium(0) nanoclusters as catalyst in decomposition of nitrous oxide.

2. Experimental

2.1. Materials

Ruthenium(III) chloride trihydrate ($RuCl_3{\cdot}3H_2O$), osmium(III) chloride hydrate ($OsCl_3{\cdot}xH_2O$), Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), sodium borohydride (98%) and sodium zeolite-Y ($Na_{56}(AlO_2)_{56}(SiO_2)_{156}{\cdot}xH_2O$) were purchased from Aldrich. Deionized water was produced from a two-step water purification system (Elix5/Milli-Q System −18.2 MΩ cm@25 °C, TOC < 10 ppb). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C.

2.2. Characterization of catalysts

The ruthenium and iron contents of prepared zeolite samples were determined by ICP–OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Leeman-Direct Reading Echelle). These analyses were performed by dissolving each sample in the mixture of nitric acid and hydrochloric acid in 1/3 ratio. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku X-ray diffractometer using Cu Kα radiation (40 kV, 30 mA) at room temperature. Scanning was performed between 0° and 55° 2θ. The measurements were made with $1°\text{min}^{-1}$ rate. The X-ray photoelectron spectroscopy (XPS) analyses were performed with Physical Electronics PHI 5000 VersaProbe using monochromatic Al Kα lines of Al (1486.6 eV, 10 mA) as an X-ray source. The FT-IR spectra of zeolite Y and catalysts were taken by Pyris 100 FT-IR spectrometer. The pellets were prepared by mixing the samples with KBr in 1/50 ratio.

2.3. Preparation of metal exchanged zeolite-Y (Ru^{+3}-Y, Fe^{+3}-Y, Os^{+3}-Y)

Ruthenium cations were introduced into zeolite Y by ion-exchange [27]. The sodium form of zeolite Y (~500 mg) was added to a solution of $RuCl_3{\cdot}3H_2O$ (~70 mg) in 100 mL H_2O in a 250 mL round bottom flask. This suspension was stirred at room temperature for 3 days. The sample was filtered by suction filtration, through Whatman 1 filter paper and washed three times with 20 mL deionized water. The filtered solid was dried under vacuum at room temperature.

Fe-Y and Os-Y catalysts were prepared by following the same ion exchange procedure [27] and using $FeCl_3{\cdot}6H_2O$ and $OsCl_3{\cdot}xH_2O$, respectively.

2.4. Preparation of intrazeolite ruthenium(0) nanoclusters

The intrazeolite ruthenium(0) nanoclusters were prepared from the reduction of Ru^{+3}-exchanged zeolite-Y with sodium borohydride following the procedure described elsewhere [28]. Ru^{+3}-Y sample (3.8 wt.% ruthenium loading, $[Ru^{+3}] = 0.02$ mM) was added into 100 mL $NaBH_4$ solution (150 mM) at room temperature. Ru^{+3} cations were reduced by $NaBH_4$ and nanoclusters were formed. $[NaBH_4]/[Ru^{3+}]$ ratio was kept over 500 to achieve complete reduction of Ru^{3+} within the cavities of Zeolite Y. When the hydrogen evolution finished (less than five minutes), the sample was filtered by suction through Whatman 1 filter paper. The filtered sample was washed three times with 20 mL deionized water to remove metaborate and chloride anions, sample was collected as black powder and transferred into schlenk tube. The tube was placed in a water bath at 70 °C and dried under vacuum. Dried samples kept in schlenk tube under vacuum at room temperature.

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