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Metal exchanged zeolites for catalytic decomposition of N_2O

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ABSTRACT

Ru + Ag/US-Y and Ru + Co/US-Y based catalysts have been studied for their catalytic activity towards N_2O decomposition, a reaction of current environmental importance. Ruthenium-cobalt based catalyst shows higher catalytic activity than the ruthenium-silver-based catalyst. Almost 90% conversion of N_2O is achieved over Ru + Co/US-Y at 583 K with a maximum of 0.134 mmol of N_2O decomposed per gram of the catalyst per unit time. These catalytic materials have been characterized for their structure, composition, morphology etc. using XRD, SEM, EDX, ICP, BET techniques. The synergistic effect of transition metals as well as chemical properties of US-Y are responsible for the excellent catalytic activity for N_2O decomposition reaction. The redox capacity of Co may also be responsible for the relatively better activity of Ru + Co based catalyst as compared to that of Ru + Ag based catalyst. These catalysts are thermally stable and can be used for the direct decomposition of N_2O emissions even under high concentration.

1. Introduction

Control of N_2O emissions has become one of the major challenges in environmental protection. N_2O is a potential contributor to the green house gases with its global warming potential (GWP) as high as 310 [1]. Different methods reported for the N_2O control at the tail gas of industries include thermal decomposition, selective catalytic reduction and catalytic decomposition. Thermal decomposition is an energy intensive method. Direct decomposition of N_2O and selective catalytic reduction of N_2O with hydrocarbons (HC-SCR) are extensively investigated as potential cost-effective technologies to remove nitrous oxide from industrial off-gases. Direct catalytic decomposition of N_2O is a relatively simple method to convert nitrous oxide in to harmless products of N_2 and O_2. It is generally believed to be more cost-effective than HC-SCR as hydrocarbons are not often present on-site and an external supply of hydrocarbons is expensive, while catalytic reduction conventionally using ammonia involves the risk of reactant slip and unwanted combustion products. It is also associated with high cost for reductant introduction.

Though, many catalysts have been studied for direct decomposition of N_2O, search for the new catalysts with improved properties is a topic of continued interest. Transition and noble metals on various supports as well as perovskites have been widely studied, but most of these catalysts are not studied at higher concentration of N_2O [2,3]. Iwamoto et al. reported the uniquely high and stable activity over exchanged Cu-ZSM-5 for the direct NO decomposition [4]. Chen et al. studied decomposition of N_2O on Cu-ZSM-5 and found that N_2O decomposition can occur on Cu-ZSM-5 at >623 K. The Cu ion is the active center for dissociative adsorption of N_2O [5]. Brink et al. reported that the catalytic decomposition of N_2O on Fe-ZSM-5 takes place at temperature above 673 K and also observed that the addition of propane lowers the temperature for N_2O conversion above 373 K [6].

Iron-zeolites, especially Fe-ZSM-5, are being studied as De-NO_x catalysts in lean-burn gasoline and diesel engines and also for N_2O decomposition and reduction. Also, high activity of Fe-ZSM-5 was observed for selective oxidations using N_2O as an oxidant, e.g. direct oxidation of benzene to phenol [7,8]. Ruthenium based catalysts on various supports have also been studied by various researchers for N_2O decomposition. Chang et al. studied the effect of Ru loading on the performance of Ru-Na-ZSM-5 catalyst for N_2O prepared by ion exchange with ruthenium content as high as 20–100% for decomposition of nitrous oxide [9]. Li and Armor also reported that Ru-ZSM-5 is

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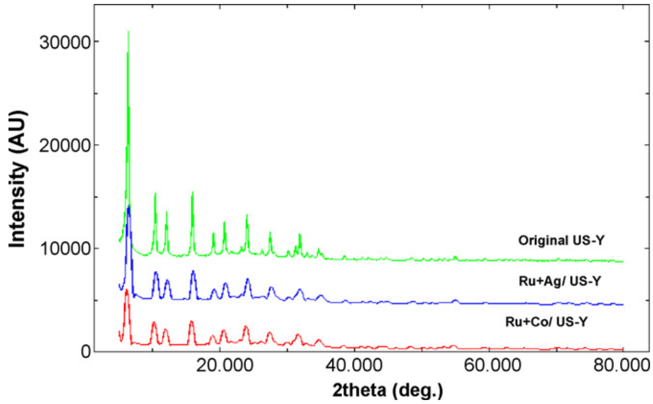

Fig. 1. XRD patterns for original US-Y, Ru + Ag/US-Y and Ru + Co/US-Y catalysts.

very active for the decomposition of nitrous oxide at low temperature [10]. Chang et al. reported decomposition of NO over Pr-, Cu-, Ga-, and Co-exchanged ZSM-5 [11]. They reported that Co-ZSM-5 containing Co in the framework had the highest activity for NO decomposition. In recent years a large number of publications are reported on catalytic approach for the control of emissions from stationary sources. Use of these catalysts in the decomposition of N_2O makes it possible to carry out the reaction at a temperature level substantially lower in comparison with the purely thermal decomposition.

In this work, we have studied the activity of Ru + Ag/US-Y and Ru + Co/US-Y, for nitrous oxide decomposition. These catalysts have been characterized with respect to their chemical composition, surface area, scanning electron micrographs (SEM), and XRD and their N_2O decomposition activity has been studied at relatively high N_2O concentrations.

2. Experimental

Commercial grade US-Y with relatively high silica–alumina ratio (Si/Al = 29) was selected as the basic material considering its better hydrothermal stability. Ru + Ag/US-Y and Ru + Co/US-Y were synthesized with targeted loading of 2.563×10^{-5} mol of ruthenium per gram and 2.878×10^{-4} mol of silver and cobalt per gram of catalysts, respectively. Ten grams of US-Y was first exchanged with $RuCl_3$ for 24 h at 303 K, then filtered and washed with deionized water to remove the chloride ions, followed by drying at 383 K for 16 h. It was then exchanged with $AgNO_3$ solution for 24 h followed by filtration and drying at 383 K. The catalyst was calcined at 723 K for 6 h. It was designated as U-1. Ru + Co/US-Y was synthesized in similar manner. After exchanging with $RuCl_3$, it was filtered, dried and then exchanged with cobalt acetate solution. This catalyst was designated as U-2.

The catalyst samples were characterized for chemical composition using both wet chemical analysis and ICP-AES technique after acid digestion. The X-ray diffraction patterns have been recorded using X-ray diffractometer, Model (Phillips: PW-1830). The radiations of Cu K_α were generated using X-ray generator of model (PW-1729) of same make and the β radiation were filtered using monochromator. The sample was scanned

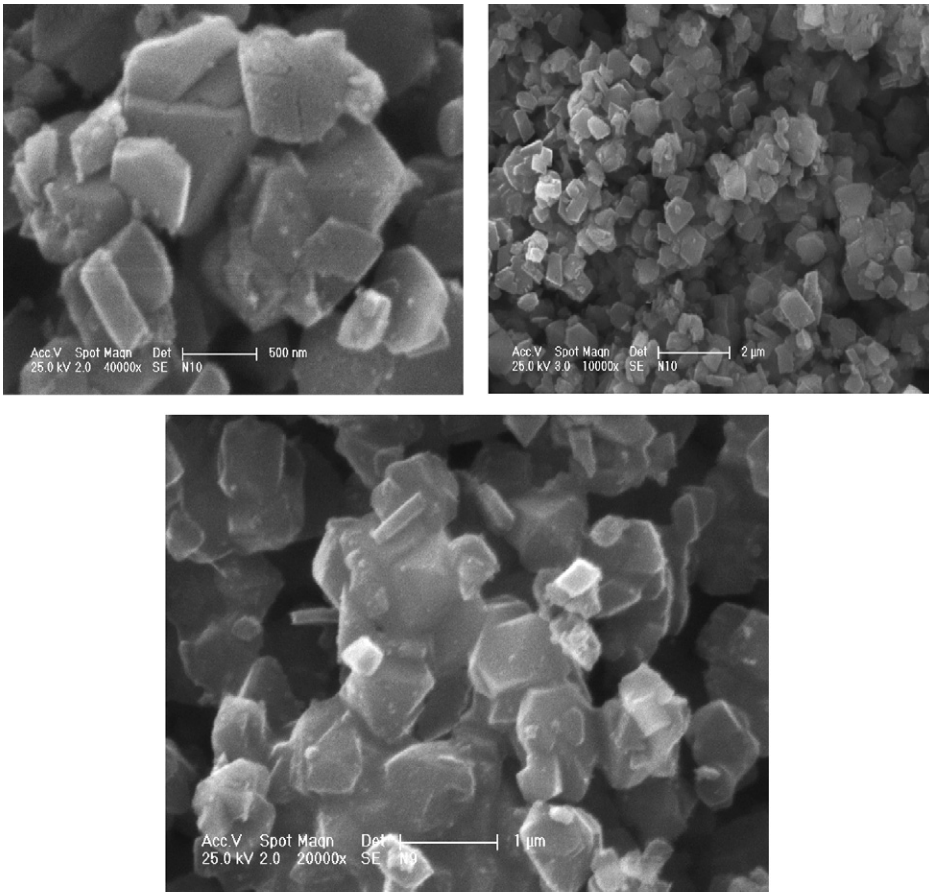

Fig. 2. SEM photograph of Ru + Co/US-Y catalyst.

for 2θ ranges from 5 to 60°. XRD data were analyzed for phase identification, presence of impurity phase, as well as for structural damage if any during the catalyst preparations. BET surface area of samples was determined following the standard nitrogen adsorption method using Micromeritics ASAP-2000 instrument. EDX analysis was performed using Philips XL 30 CP. The sample was placed on an adhesive C slice and coated with Au–Pd alloy 10 nm thick layer. The aim of this analysis was to get information about the presence and distribution elements on the external surface of the samples.

2.1. Catalytic evaluations

The catalytic decomposition of N_2O was carried out in a fixed-bed reactor under steady state conditions. Catalyst sample (≈0.1 g) was diluted with the same size and amount of quartz beads and placed in a quartz reactor for catalytic run. Prior to the catalyst testing, the catalysts were pretreated at 673 K for 2 h in a flow of helium to stabilize the catalysts. The flow rate of high purity N_2O (5000-PPM in He) gas was measured by mass flow controllers (Albourg, USA). The total flow rate used for each run was 60 ml min^{-1} thereby yielding a space velocity of 36,000 h^{-1}. After the catalyst had attained steady state over a period of 30 min at each temperature, the effluent gas was analyzed by a micro gas-chromatograph (Varian CP-4900 TCD) using a Molecular Sieve 5A column (for the analysis of O_2, N_2) and a Porapak column as well as by a chemiluminiscence NOx analyzer (Environment SA).

The catalytic activity was evaluated in terms of conversion (X) of N_2O gas according to the following equation:

$$X_{N_2O} = \frac{P_{N_2O\ \text{in}} - P_{N_2O\ \text{out}}}{P_{N_2O\ \text{in}}}$$

3. Results and discussion

The original US-Y has high $SiO_2/Al_2O_3 = 29$ ratio, which is responsible for its hydrothermal stability. However, the alumina content is enough for the cation exchange capacity to introduce catalytically active metal ions. The X-ray diffraction patterns of U-1, U-2, show intact structure of zeolites-Y after the ion-exchange experiments. It was not possible to identify the presence of metal oxide due to its low content and high dispersion through ion exchange (Fig. 1). The scanning electron micrographs (Figs. 2 and 3) show the surface morphology of Ru + Ag/US-Y and Ru + Co/US-Y powder prepared by ion-exchanged method. The SEM micrographs show that the powders obtained by ion-exchange method contain particles typical of US-Y. EDX analyses of samples Ru + Co/US-Y and Ru + Ag/US-Y (Figs. 4 and 5, respectively) confirm the presence and excellent dispersion of ruthenium, silver and cobalt zeolites phases. As expected, there is practically no change in the morphology of zeolite samples after the ruthenium, silver and cobalt incorporation. The BET surface area results of catalysts are shown in Table 1, which suggest the high surface area of catalytic materials even after calcination at higher temperature. There seems to be no impact of metal loading on surface area, which, also indicates

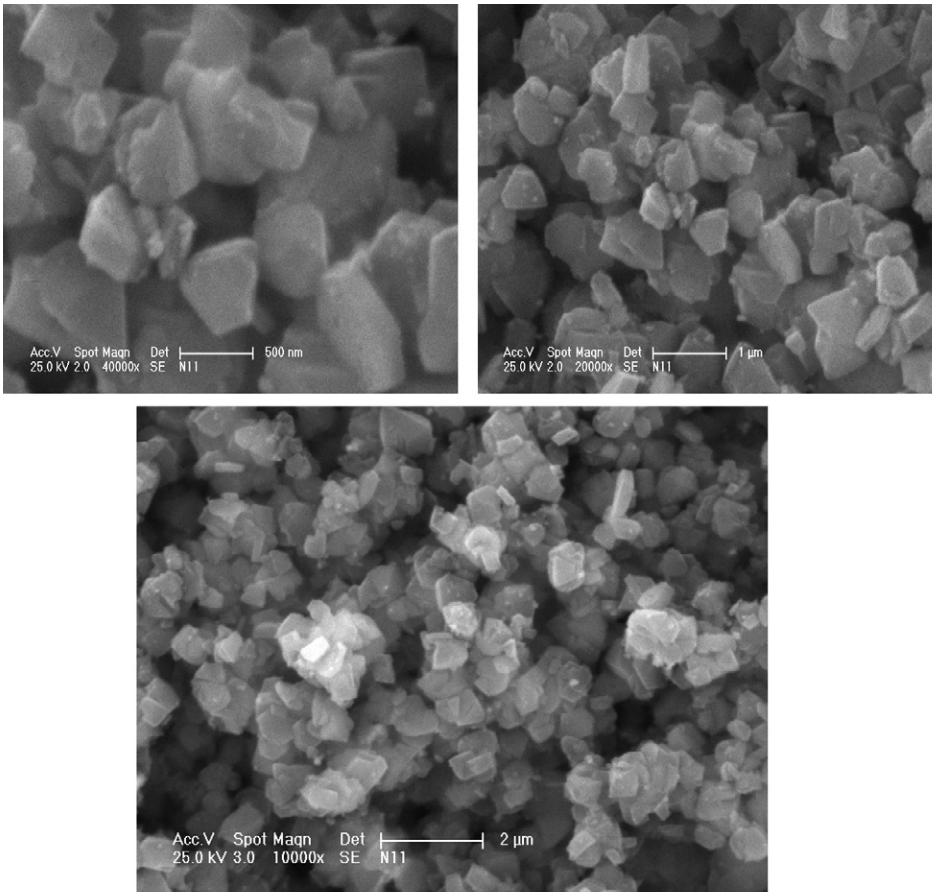

Fig. 3. SEM photograph of Ru + Ag/US-Y catalyst.

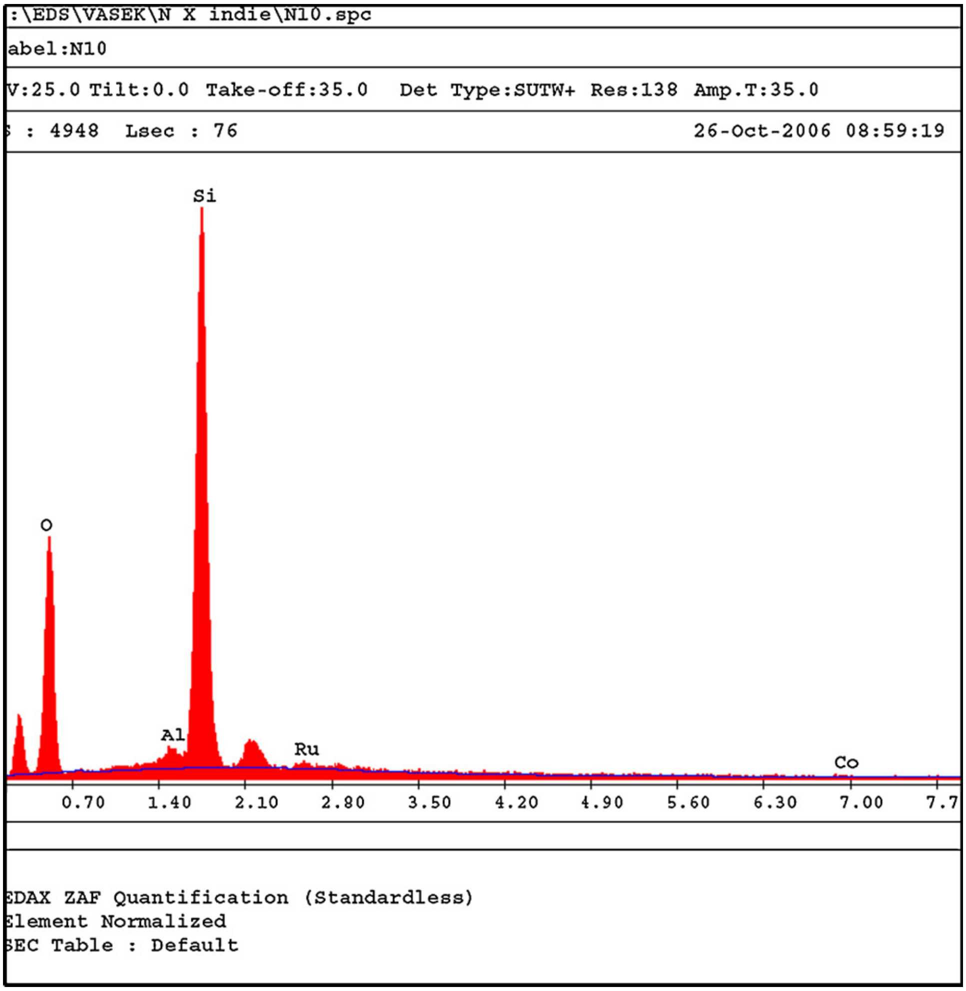

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Fig. 4. EDX pattern for Ru + Co/US-Y catalyst.

the high dispersion of metals on exchange sites of zeolites, and ruling out the possibility of pore blockage if any.

The catalytic activity results for Ru + Ag/US-Y and Ru + Co/US-Y catalysts are presented in Fig. 6. Commercial US-Y does not show any significant activity for N_2O decomposition. The light-off temperature for Ru + Co/US-Y (U-2) is around 483 K and reaches T_{90} at 583 K, whereas for the Ru + Ag/US-Y, the reaction starts at around 573 K followed by a steep rise in activity in a temperature window of 543–623 K. However, the T_{90} was observed at about 683 K. This indicates the overall much better catalytic activity of Ru + Co/US-Y and a promotional effect of cobalt ions. Fig. 7 shows change in turn over frequency (TOF) vs. temperature. TOF is calculated as millimoles of N_2O converted per gram of catalyst per unit time. Maximum 0.134 mmol of N_2O are converted per gram of catalyst per min when U-2 shows the maximum conversion at 613 K. U-1 converts a maximum of 0.134 mmol of N_2O at about 773 K. Both the catalysts show overall excellent catalytic activity for the N_2O control reaction.

Table 1
BET surface area results

Serial number	Code	Sample composition	Surface area (m^2/g)
1	US-Y	Original US-Y	568.71
2	U-1	Ru + Ag/US-Y	501.41
3	U-2	Ru + Co/US-Y	527.42

There are several reaction mechanisms proposed for the catalytic decomposition of N_2O. Decomposition of N_2O on the catalyst takes place probably on a redox mechanism. N_2O acts as an oxidizing agent and oxygen is desorbed in the reducing step. During the pretreatment at high temperature, cobalt and silver are expected to be reduced to Co^{2+} and Ag^0, which are then oxidized by N_2O to Ag^+ and Co^{3+} and consequently N_2O gets reduced to nitrogen and oxygen. Another possible mechanism for the decomposition of N_2O on ruthenium site is donation of electrons from the surface to ruthenium sites which causes the ruthenium cations to become electron rich, which in turn, lead to electron transfer to N_2O resulting in weakening of the N–O bond (10). Cleavage of N–O bond may be the rate limiting step for this reaction, while desorption of oxygen from the catalyst surface may also require considerable energy. The better activity of cobalt based catalyst could be due to its better redox capacity and therefore a synergistic effect of Ru and Co is probably responsible for the overall excellent activity for the decomposition N_2O. It was not possible to characterize the metal phases present on the catalysts, as there could also be a possibility of the formation of nano-particles of metal oxides with preferential formation of certain crystal planes. These metal oxide particles are therefore, expected to have different electronic properties leading to different catalytic properties as well. Further characterization of these catalysts is under progress which may lead to some conclusive information related to mechanistic aspects.

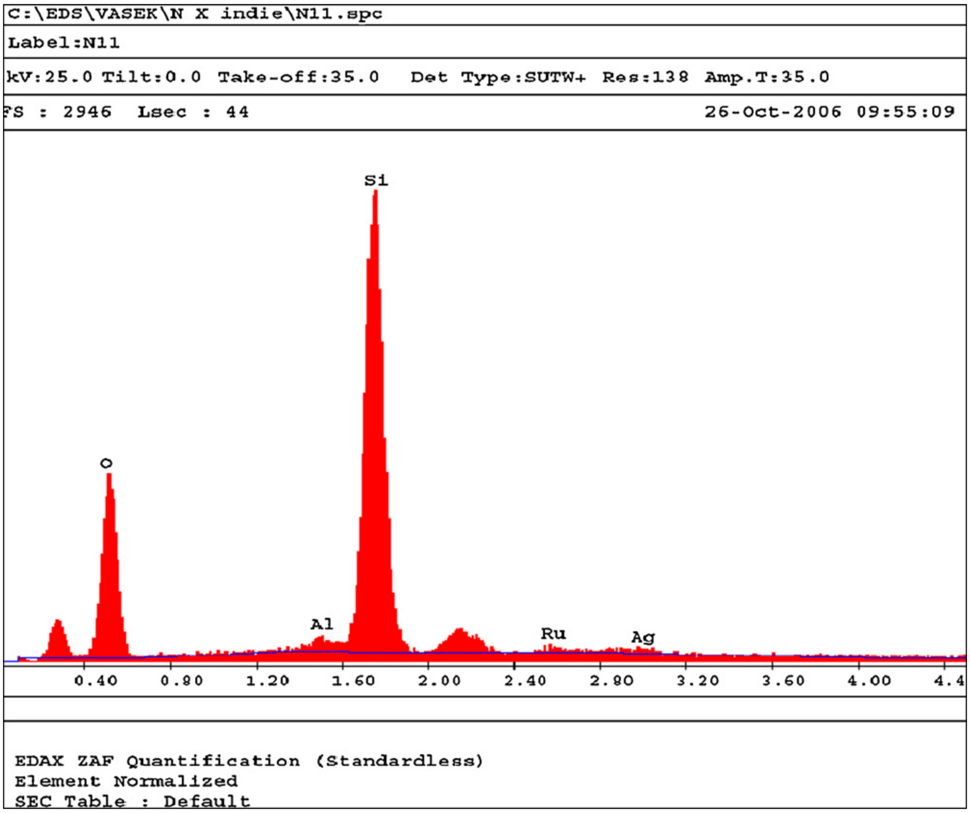

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Fig. 5. EDX pattern for Ru + Ag/US-Y catalyst.

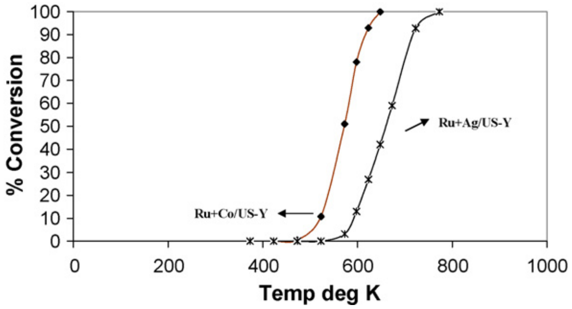

Fig. 6. N_2O decomposition vs. temperature for Ru + Co/US-Y and Ru + Ag/US-Y.

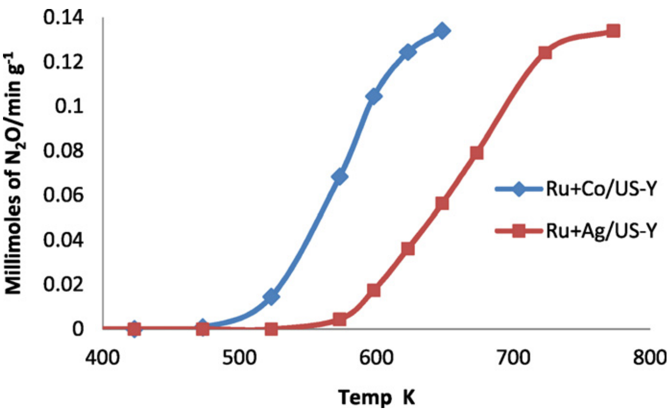

Fig. 7. Turn over number (TON) vs. temperature for Ru + Co/US-Y and Ru + Ag/US-Y.

4. Conclusion

Zeolite based bimetallic catalysts with compositions Ru + Co and Ru + Ag have been synthesized by ion-exchange method, and studied for their N_2O decomposition activity. Ion-exchange method results in excellent dispersion of metals in US-Y and does not affect its crystallinity, if pH of the solution is maintained properly during the synthesis. Although, both the catalysts show excellent catalytic activity for the N_2O decomposition reaction, however, Ru + Co based catalyst is relatively better and it was possible to get over 90% N_2O decomposition at 583 K. This is an excellent activity under the conditions of experiment and deserves further investigations.

The better activity of Ru + Co/US-Y catalyst could be due to the redox capacity of Co, while Ru sites probably offers sites for N_2O decomposition. Hydrothermally stable US-Y with high SiO_2/Al_2O_3 ratio appears to be an excellent support for the high dispersion of active metals like ruthenium, silver and cobalt, while their catalytic properties can also be tailored by structural modifications. Their surface area is also equally responsible for their high catalytic activity, while their low cation exchange capacity, could be useful for the dilute and uniform dispersion of active cations.

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