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An investigation into the effect of Cs promotion on the catalytic activity of NiO in the direct decomposition of N_2O

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A series of Cs promoted NiO catalysts have been prepared and tested for direct decomposition of N_2O. These catalysts are characterized by BET surface area, X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption of N_2O (TPD-N_2O) and X-ray photo electron spectroscopy (XPS). The Cs promoted NiO catalysts exhibit higher activity for the decomposition of N_2O compared to bulk NiO. The catalyst with Cs/Ni ratio of 0.1 showed highest activity. The enhancement in catalytic activity of the Cs promoted catalysts is attributed to the change in the electronic properties of NiO. The characterization techniques suggest weakening of Ni–O bond thereby the desorption of oxygen becomes more facile during the reaction. The Cs promoted NiO catalyst is effective at low reaction temperature and also in the presence of oxygen and steam in the feed stream.

KEY WORDS: N_2O decomposition; nickel oxide; cesium promoter.

1. Introduction

Nitrous oxide pollution abatement is an important environmental problem due to the high greenhouse potential of the gas and its ozone-depleting property [1]. The emission of N_2O comes from not only natural sources but also human contributions such as the production of adipic acid and nitric acid [2] and fluidized bed combustors for sewage-sludge or industrial wastes [3]. One of the often recommended options is the direct catalytic decomposition of N_2O to N_2 and O_2 as it does not require usage of an additional reductant. The decomposition reaction has been studied extensively over various catalysts such as noble and non-noble metals, mixed metal oxides and ion exchanged zeolites [4–7]. However, most of the catalytic systems are not efficient for the commercial exploitation [1,8]. The most active catalysts for N_2O decomposition consist of metal exchanged zeolites [6,9] or mixed metal oxides [10]. The main problem with the decomposition catalysts is that their activities are severely inhibited by the presence of oxygen and water vapor. The oxygen formed during the reaction adsorbs strongly on the catalyst surface leading to inhibition of the rate. In a recent communication it has been reported that nano-Au supported on Co_3O_4 is a highly active catalyst for N_2O decomposition [11]. However, the preparation of this catalysts is critical and is not desirable for commercial applications as it involves usage of expensive metal such as gold.

Even though NiO is used as a catalyst and support for various reactions such as the oxidative dehydrogenation of lower alkanes, methane-reforming etc. [12], it has not been explored much for N_2O decomposition. Recently, Ohnishi *et al.* have reported about the activity of NiO catalysts for N_2O decomposition [13]. Their main study is on the alkali promoted Co_3O_4 catalysts. A comparison is made among some of the bulk metal oxides including NiO for N_2O decomposition activity. However, the influence of Cs promotion on NiO catalyst is not focused. Besides, the effect of oxygen and steam on N_2O decomposition has not been attempted. We observed that by suitable modification with alkali metal ions NiO catalysts could be made highly active for N_2O decomposition. In the present investigation, an attempt has been made to understand, the role of Cs as a promoter for NiO in direct decomposition of N_2O. The effect of the presence of excess oxygen and water vapor in the reaction mixture is investigated. The reasons for improved activity and stability are also explored.

2. Experimental

A series of Cs promoted NiO catalysts were prepared by conventional simple techniques. $Ni(OH)_2$ was first precipitated from an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ by the addition of required amount of aqueous Na_2CO_3, at room temperature until the pH reached a value of 10. The precipitate thus obtained was washed with distilled water, dried at 120 °C and then

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calcined at 400 °C for 4 h in flowing air. Cs was added to NiO by impregnation with an aqueous solution of cesium nitrate, followed by drying at 120 °C. All the catalyst samples were finally calcined at 600 °C for 5 h in flowing air. The Cs to Ni atomic ratio was varied from 0.05 to 0.2.

The specific surface area of the catalyst samples were estimated using N_2 adsorption at −196 °C by the single-point BET method on a Micromeritics Chemisorb 2700 instrument. The samples were oven-dried at 120 °C for 12 h and flushed *in situ* with He gas for 2 h before the measurements.

X-ray powder diffraction patterns were recorded on a Siemens D5000 diffractometer, using Cu Kα radiation (1.5406 Å) at 40 kV and 30 mA and a secondary graphite monochromator. The measurements were obtained in steps of 0.045° with a count time of 0.5 s and in the 2θ range of 2–80°. Identification of the solid phase was made with the help of JCPDS files.

Temperature programmed reduction (TPR) of the catalysts was carried out in a flow of 10% H_2/Ar mixture gas at a flow rate of 30 mL/min with a temperature ramp of 10 °C/min. Before the TPR run the catalysts were pretreated in argon at 300 °C for 2 h. The hydrogen consumption was monitored using a thermal conductivity detector.

Temperature programmed desorption of N_2O was performed in a fixed-bed flow reactor interfaced with a micro gas chromatograph (Varian CP-4900). Prior to the experiment, the catalyst sample was pretreated in H_2 flow (30 mL/min) at 400 °C for 1 h. After this the sample was flushed with He gas at the same temperature for 1 h and cooled to room temperature in He flow. The sample was exposed to 5,000 ppm N_2O (balance He) gas for 1 h at room temperature, followed by flushing with He until no N_2O was observed in the vent gas. After these treatments the N_2O-TPD was carried out in a flow of He (80 mL/min) with a heating rate of 5 °C/min.

The X-ray photo electron spectroscopy (XPS) measurements of the catalysts were conducted on a Kratos Axis 165 apparatus equipped with a dual anode (Mg and Al) using a MgK_α source. The carbon 1s binding energy of 284.6 eV was used as a reference for determining the binding energies. A charge neutralization of 2 eV was used to balance the charge up of the sample. The binding energy values of the samples were reproducible within ±0.1 eV.

The direct decomposition of N_2O was carried out in a fixed-bed continuous flow reactor. The reactant mixture consisted of one or more of 2500 ppm N_2O, 4% O_2 and 2% H_2O along with He as the diluent. The gas mixture was passed over a 0.5 g catalyst at a total flow rate of 60 mL/min. The effluent gas was analyzed by micro-gas chromatography using molecular sieve and poroplot Q columns. The steady-state catalytic activity was measured at temperatures between 200 and 550 °C, in steps of 50 °C.

3. Results and discussion

The physico-chemical properties of bulk NiO and Cs promoted NiO catalysts are presented in table 1. The BET surface area of the bulk catalyst is very low. The addition of small amount of Cs leads to increase in surface area up to Cs/Ni = 0.1 followed by a continuous decrease with further increase in Cs content.

The X-ray diffraction (XRD) patterns of the fresh catalysts are shown in figure 1. The patterns suggest the presence of crystalline NiO in all the catalysts. However, in the case of promoted catalysts peaks with smaller intensity (which match with those of the data given in JCPDS file No. 10-0248) corresponding to Cs_2O_3 are seen, particularly in catalysts with high Cs content.

The TPR profiles of the bulk NiO and Cs promoted NiO catalysts are shown in figure 2. The bulk NiO shows a single and broad reduction peak around 400 °C related to the single step reduction of Ni^{2+} to Ni^0. The addition of Cs, particularly in small quantities (Cs/Ni = 0.05 and 0.1), the peak splits into two indicating a two-stage reduction of NiO. In the case of catalyst with Cs/Ni = 0.1, the first peak consisting of a major portion, appears at lower temperature. The TPR results suggest that the presence of small amount of Cs is

Table 1
Physico-chemical properties of unpromoted and Cs promoted NiO catalysts

Catalyst	Cs/Ni ratio	B.E.T surface area (m^2/g)	Cs/Ni ratio[a]
NiO	–	5.7	–
Cs/Ni = 0.05	0.05	10.6	0.052
Cs/Ni = 0.10	0.10	4.6	0.102
Cs/Ni = 0.15	0.15	3.7	0.153
Cs/Ni = 0.20	0.20	3.5	0.250

[a] Calculated from XPS analysis.

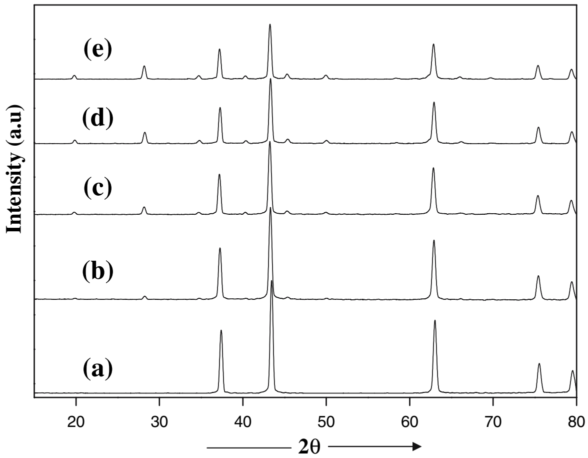

Figure 1. XRD patterns of fresh catalysts (a) Bulk NiO (b) Cs/Ni = 0.05 (c) Cs/Ni = 0.1 (d) Cs/Ni = 0.15 (e) Cs/Ni = 0.2.

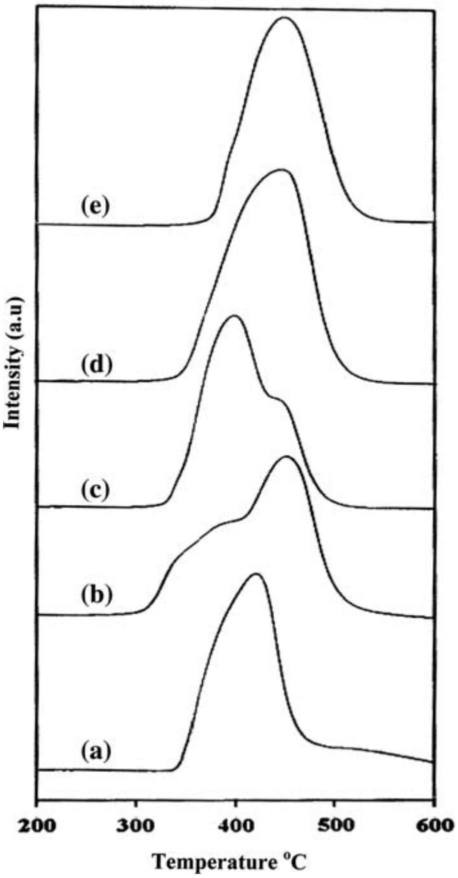

Figure 2. TPR patterns of fresh catalysts (a) Bulk NiO (b) Cs/Ni = 0.05 (c) Cs/Ni = 0.1 (d) Cs/Ni = 0.15 (e) Cs/Ni = 0.2.

effective in stabilizing the lower oxidation state of Ni. This trend is indicative of an electronic promoting function of cesium [14]. Further increase in Cs content has moved the NiO reduction peak to high temperatures. Literature reveals that at high concentrations Cs migrates to Ni surface leading to reduction inhibiting counter effect [15]. A similar phenomenon might be occurring in the present catalyst as well.

The variation in the decomposition activity in terms of N_2O conversion over bulk NiO and Cs promoted NiO catalysts, at a typical reaction temperature of 250 °C, is presented in figure 3. The bulk NiO catalyst shows very low conversion at 250 °C whereas the conversion increased substantially with the addition of Cs to NiO. At a Cs/Ni atomic ratio of 0.1, the catalyst has exhibited 100% N_2O conversion. Thus, the N_2O decomposition activity seems to be a function of ease of reducibility of NiO, promoted by the presence of Cs and keeping Ni in its lower oxidation state. Further increase in Cs content has lead to decrease in the N_2O decomposition activity.

XPS analysis was carried out to throw more light on the influence of Cs on NiO in enhancing the N_2O decomposition. The Ni $2P_{3/2}$ binding energies of bulk NiO and Cs promoted NiO are obtained as 855.46 and 855 eV, respectively. The addition of Cs to NiO leads to decrease in the B.E. It is well known that electron donation from alkali metals to transition metals takes place at the interface resulting in a decrease of the work function and then a translation of the whole system towards a lower B.E [16]. A similar type of shift in the B.E value has been reported for Na promoted Pd/SiO_2 catalyst [17]. The decrease in the peak maximum of the NiO reduction in the TPR patterns with the addition of Cs also supports this observation. The reduction in B.E value indicating a change in the electronic state of Ni means that the Ni–O bond is weakened upon the addition of Cs. The presence of small amount of Cs enhances the adsorption of N_2O at the interface of Cs and NiO. All these factors are in support of the observed high activity of the Cs promoted NiO catalyst up to Cs/Ni ratio of 0.1. The decrease in activity with further addition of Cs, can be ascribed to migration of Cs to the surface thus lowering the available NiO sites for N_2O decomposition. The atomic ratio of Cs/Ni as measured by XPS (table 1) for high Cs/Ni = 0.2 catalyst is found to be 0.25. This ratio is higher than the theoretical value (0.2) and supports the concept of migration of Cs on to the surface of Ni.

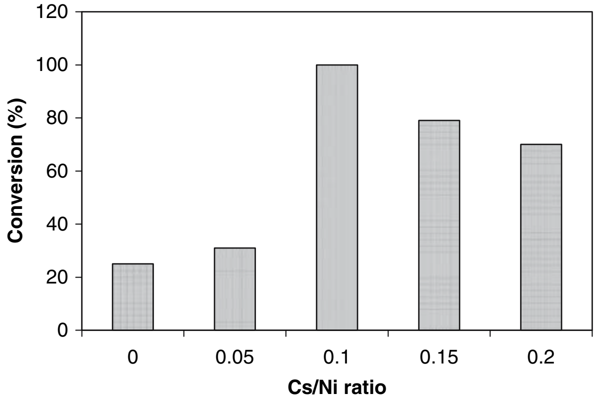

Figure 3. N_2O decomposition activity over the bulk NiO and Cs promoted NiO catalysts.

The most active Cs promoted NiO (Cs/Ni = 0.1) catalyst along with bulk NiO are studied for time on stream analysis in order to measure their stability during N_2O decomposition. A continuous testing of these two catalysts is carried at 350 °C and the results are shown in figure 4. It is noteworthy that the Cs promoted catalyst has exhibited a stable activity during the entire time of operation. However, the bulk NiO catalyst has started deactivating after 3 h of operation. This might be due to the accumulation of oxygen on the surface of NiO.

As discussed above, the high activity of the promoted NiO catalyst might be due to a change in the electronic structure whereby the release of adsorbed O_2 becomes facile. In order to explore this phenomenon further TPD of N_2O has been carried out on the two catalysts. The TPD patterns obtained on bulk NiO and Cs promoted

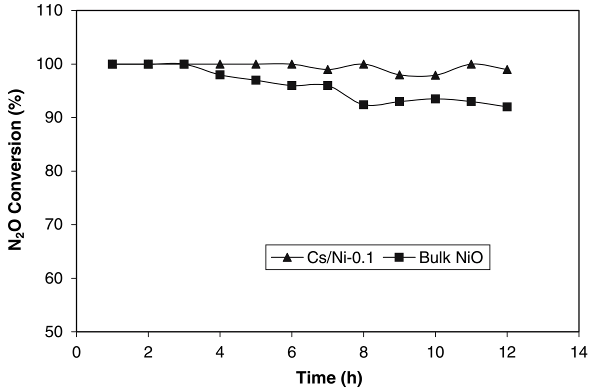

Figure 4. Time on stream analysis on NiO bulk and Cs promoted NiO (Cs/Ni = 0.1) catalysts (a) Bulk NiO (b) Cs/Ni = 0.1 catalysts.

NiO (Cs/Ni = 0.1) catalysts are shown in figure 5. The Cs promoted catalyst shows the release of N_2O decomposition products, *viz*., O_2 and N_2 at lower temperature when compared to bulk NiO catalyst. The sharp and early desorption of O_2 (at 300 °C) can be ascribed to the reduction in the strength of Ni–O bond due to the addition of Cs to NiO. It is interesting to see that the three N_2 desorption peaks are very distinct in the case of alkali promoted NiO catalyst. The first low temperature desorption peak can be attributed to the N_2 produced by N_2O dissociation. The second and third desorption peaks might be a result of the decomposition of a nitrate complex formed during TPD of N_2O. The nitrate is formed via nitric oxide, which in turn is formed from N_2O and surface oxygen atom. The existence of nitrate species during decomposition of N_2O is already reported [18]. Similar observations are also made over Ba/MgO catalysts [19]. Haneda *et al*., reported the weakening of Co–O band due to the presence of alkali metal [20]. They have also noticed early release of oxygen with a strong and sharp O_2 desorption peak in the O_2-TPD on alkali promoted CoO_3 catalysts.

The effect of oxygen and steam on N_2O decomposition over the NiO and Cs promoted NiO catalysts are studied at different temperatures and the results are shown in figure 6. The bulk NiO shows complete N_2O decomposition in the range of 250–350 °C when N_2O is alone present in the feed stream. In the presence of O_2 or H_2O, the N_2O decomposition curve has shifted to higher temperatures. These shifts suggest the inhibition effect of steam and oxygen on N_2O decomposition. In the case of Cs promoted NiO catalyst (Cs/Ni = 0.1) when N_2O is

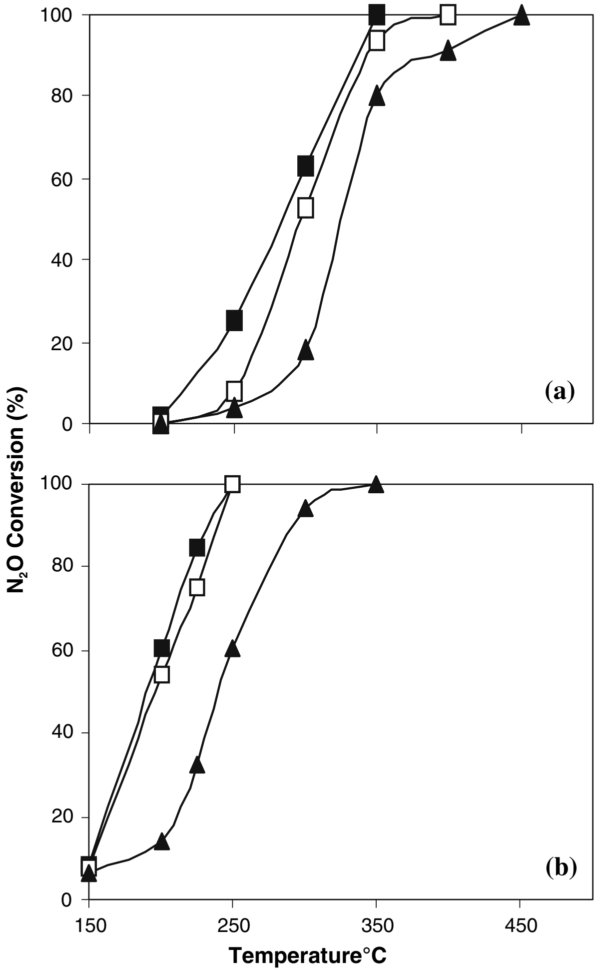

Figure 6. N_2O decomposition to N_2 and O_2 over (A) Bulk NiO and (B) Cs/NiO = 0.1 catalysts at different feed compositions: (■) 2500 ppm N_2O; (□) 2500 ppm N_2O + 4%O_2 and (▲) 2500 ppm N_2O + 2% H_2O.

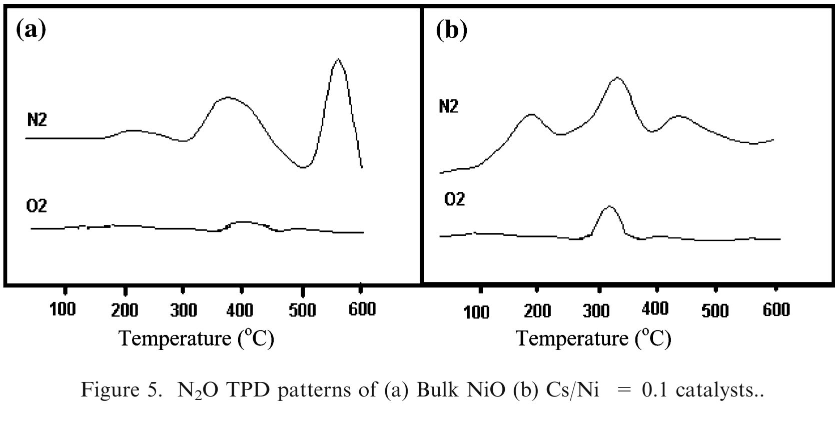

Figure 5. N_2O TPD patterns of (a) Bulk NiO (b) Cs/Ni = 0.1 catalysts..

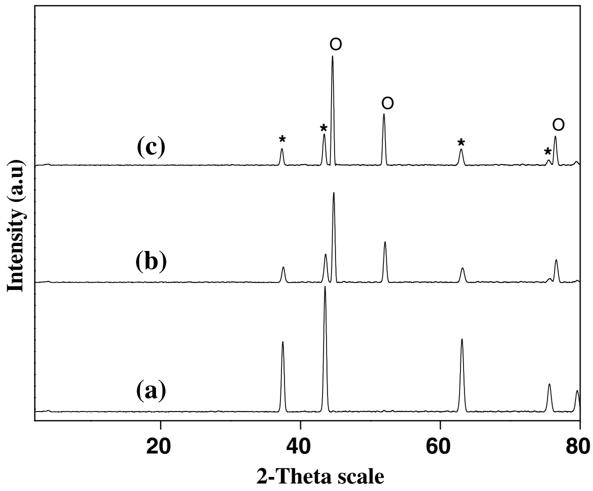

Figure 7. XRD patterns of the used catalysts (a) Bulk NiO (N_2O + O_2); (b) Cs/NiO (N_2O + O_2) (c) Cs/NiO (N_2O + O_2 + H_2O). (*) = NiO; (O) = Metallic Ni.

the only reactant, the N_2O decomposition curve has shifted to about 100 °C lower side compared to that of the bulk NiO catalyst. The presence of O_2 has not made much difference in N_2O decomposition activity indicating that O_2 does not compete with N_2O adsorption sites in Cs/NiO catalysts. Generally, the oxygen atoms formed during the decomposition of N_2O accumulate on the catalyst surface and lead to decrease in activity [21]. In the present case such a decrease is not noticed. As reported earlier, the TPD of N_2O obtained on the same catalyst suggests an early and easy desorption of oxygen from the surface revealing that this catalyst is not deactivated by the presence of oxygen. A slight shift in N_2O decomposition curve, in the presence of H_2O, to higher temperature compared to the curve obtained in the presence of O_2 suggests that water is adsorbed on active sites leading to inhibition of decomposition. This effect is pronounced at lower temperatures, which needs to be further examined.

In order to understand the higher activity and stability of the promoted catalyst compared to that of the unpromoted one, XRD characterization has been carried out on the samples collected after reaction. These patterns are shown in figure 7. The XRD of the bulk NiO catalyst after N_2O decomposition in presence of O_2 shows patterns related bulk NiO, whereas in the case of Cs promoted NiO catalyst the presence of metallic Ni phase is predominant. This result suggests that the re-oxidation of Ni, by excess oxygen present in the reaction mixture, is hindered by the presence of Cs. The retention of Ni phase might be the reason for its high activity in the presence of O_2.

In conclusion, it can be stated that Cs promoter reduces the Ni–O bond strength, which in turn helps easy desorption of oxygen formed during the decomposition due to stabilization of Ni in its lower oxidation state. The promoted catalysts are more active and better resistant to oxygen and water vapor in feed stream.

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