

Direct Decomposition of N₂O over Cesium-doped CuO Catalysts

Nayem Pasha · N. Lingaiah · P. Siva Sankar Reddy ·
P. S. Sai Prasad

Received: 1 May 2008 / Accepted: 2 September 2008 / Published online: 7 October 2008
© Springer Science+Business Media, LLC 2008

Abstract A series of Cs promoted copper oxide catalysts were prepared by co-precipitation method and tested for the direct decomposition of nitrous oxide (N₂O). The Cs promoted catalysts were more active particularly with a molar ratio of Cs/Cu at 0.1 compared to bulk CuO. Methods of XRD, BET, XPS, H₂-TPR, and N₂O-TPD were used to characterize these catalysts to evaluate structure activity relationship. The characterization results indicated that the addition of Cs could improve the reduction of Cu²⁺–Cu⁰ by facilitating the desorption of adsorbed oxygen species, during the N₂O decomposition. The influences of oxygen and steam on N₂O decomposition over these catalysts were also studied.

Keywords Nitrous oxide · Copper oxide · Cesium · Decomposition

1 Introduction

Nitrous oxide (N₂O) is a greenhouse gas with a long lifetime of about 150 years in the atmosphere [1, 2]. Although N₂O is not the major contributor to global warming, it is much more potent than either of the other two most common anthropogenic greenhouse gases, CO₂ and CH₄. N₂O is 310 and 21 times of the Global warming potential (GWP) of CO₂ and CH₄, respectively [1, 3]. Furthermore, N₂O is an important source of stratospheric nitrogen

oxides, which initiates a chain of cyclic reaction leading to stratospheric ozone destruction [1–4].

It is emitted from both natural and anthropogenic sources such as nitric acid and adipic acid plants and fluidized bed combustors for sewage-sludge or industrial wastes besides the medical exhaust biological and agricultural emissions [5]. The concentration of N₂O in the atmosphere continues to increase, and this increase appears to be caused mainly by human activities. With increasing concerns about protecting our environment, the catalytic removal of N₂O from exhaust becomes at most important. It was reported that N₂O is easily decomposed to nitrogen and oxygen on various types of catalysts such as noble metals [5–7], metal oxides [8–12], and ion-exchanged zeolites [13–15]. However, few of them have been found to be active and stable enough for industrial applications, because their activities are severely inhibited by the presence of other gases such as O₂. Moreover, oxygen atoms formed by the decomposition of N₂O are hardly desorbed from the catalyst surface and accumulated on the surface, finally causing catalyst deactivation [5, 16].

Catalysts with copper oxide as an active component have been extensively employed in the recent past for the selective catalytic reduction of NO_x and also for the synthesis and steam reforming of methanol [17–21]. Copper catalysts are very selective in hydrogenation–dehydrogenation reactions such as conversion of benzaldehyde to benzyl alcohol [17, 22], furfural to furfuryl alcohol [23] or the transformation of alcohols into their corresponding aldehydes or ketones [24–26]. Copper based catalysts for direct decomposition of N₂O–N₂ have been reported [27, 28]. Most of the catalysts are supported ones where Cu is supported on metal oxides and perovskites [29–35]. Zeolite supported Cu catalysts are also studied for N₂O decomposition [36, 37]. There are no studies about the alkali

N. Pasha · N. Lingaiah · P. S. S. Reddy · P. S. S. Prasad (✉)
Catalysis Laboratory, Inorganic and Physical Chemistry
Division, Indian Institute of Chemical Technology,
Hyderabad 500607, India
e-mail: saiprasad@iict.res.in

promoted catalysts for this reaction. Generally alkalis promoted metal oxides exhibit better activity toward N_2O decomposition at low reaction temperatures.

In the present paper, we report the catalytic performance of a Cs metal-doped catalyst for N_2O decomposition. The effects of oxygen and steam on N_2O decomposition are also studied. Discussions are made on the relationship between catalytic performance and structural properties revealed by characterization of catalysts.

2 Experimental

A series of Cs promoted CuO catalysts were prepared by conventional techniques. $\text{Cu}(\text{OH})_2$ was first precipitated from an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 calcined at 400 °C for 4 h in flowing air. Cs was added to CuO by impregnation with an aqueous solution of cesium nitrate. The excess solution was removed on hot plate, followed by drying at 120 °C. All the catalyst samples were finally calcined at 450 °C for 5 h in flowing air. The Cs to Cu atomic ratio was varied from 0.05 to 0.2.

The specific surface areas 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 diffract meter, using $\text{CuK}\alpha$ radiation (1.5406 Å) at 40 kV and 30 mA and secondary graphite monochromatic. The measurements were obtained in steps of 0.045° with a count time of 0.5 sec and in the 2θ of 2 – 80° . Identification of the solid phase was made with the help of JCPDS files.

Temperature programmed reduction 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 10 °C/min.

The XPS measurements of the catalysts were conducted on a Kratos Axis 165 apparatus equipped with a dual anode (Mg and Al) using a $\text{MgK}\alpha$ source. The carbon 1 s 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 2,500 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

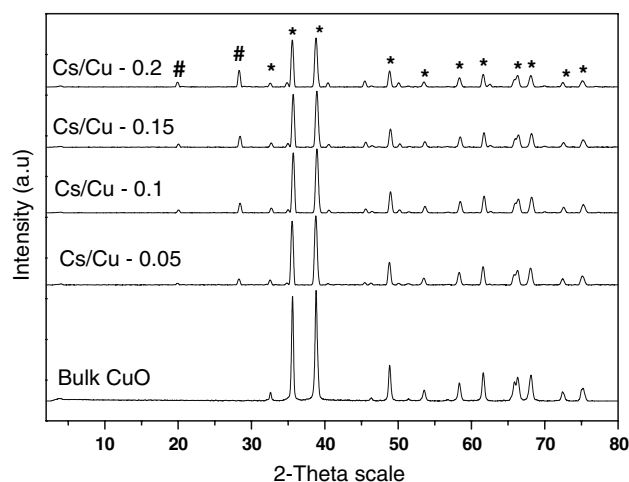
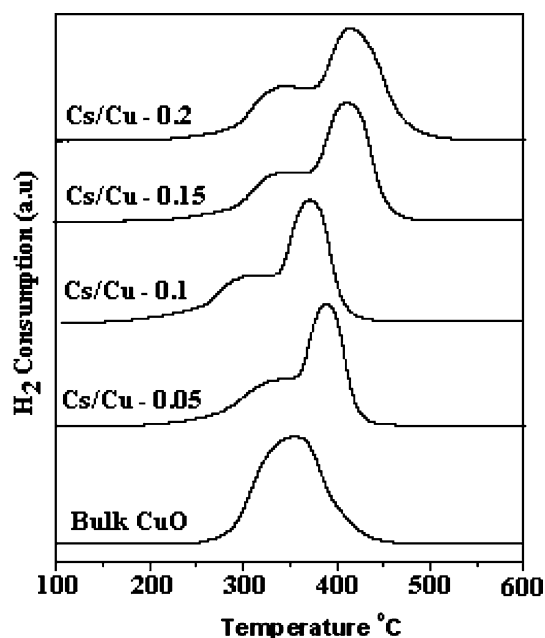
The physico-chemical properties of bulk CuO and Cs promoted Cu catalysts are presented in Table 1. The BET surface area of the bulk CuO and Cs promoted CuO are very low.

XRD patterns of the bulk CuO and Cs promoted CuO with different Cs/CuO ratios are shown in Fig. 1. XRD pattern of the samples shows the characteristic peaks of CuO with 2θ values at 32.4, 35.6, 38.6, 48.8, 53.5, 58.4, 61.6, 66.1, and 68.1 [38]. At higher Cs/Cu ratios, peaks due to the crystalline Cs_2O_3 phases are noticed, in addition to CuO. The intensity of these peaks was found to increase with increase in Cs loading. The XRD patterns suggest that at higher Cs content the crystallites of Cs_2O_3 are formed on the surface of CuO.

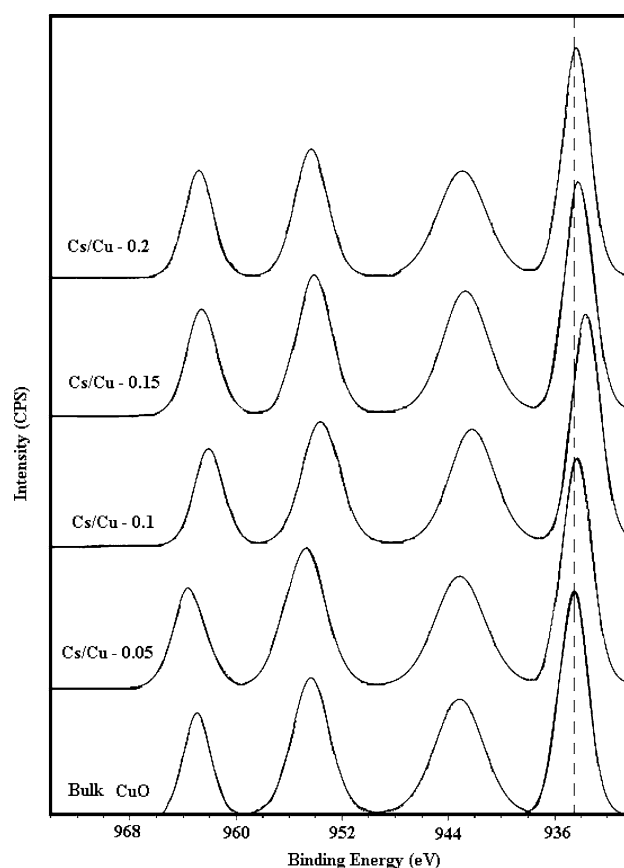
TPR profiles of bulk CuO and Cs doped CuO are shown in Fig. 2. The bulk CuO shows a single and broad reduction peak at around 350 °C related to the single step reduction of Cu^{2+} – Cu^0 . Cs doped CuO, consists of two well-resolved reduction peaks at around 300–340 and 400–450 °C. According to the literature [39–41], the low-temperature peak can be ascribed to the reduction of Cu^{2+} – Cu^{1+} ; while the higher one is due to the reduction of Cu^{1+} to Cu^0 . As the Cs content increased the reduction peak related Cu^{1+} – Cu^0 shifted to high temperature. The low temperature peak is not varied for the very low Cs content i.e., upto 0.1 and above this content both the low and high temperature reduction peaks are shifted to higher temperatures. The TPR results suggest that the presence of small amount of Cs is effective in stabilizing the lower oxidation

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

Catalyst	Cs/Cu ratio	BET surface area (m ² /g)	Cs/Cu ratio ^a	Cs/Cu ratio ^b
CuO		0.84	–	–
Cs/Cu = 0.05	0.05	0.28	0.045	0.047
Cs/Cu = 0.1	0.10	0.40	0.088	0.09
Cs/Cu = 0.15	0.15	0.54	0.14	0.13
Cs/Cu = 0.2	0.20	0.72	0.18	0.22

^a Calculated from XPS analysis^b Calculated from ICP analysis**Fig. 1** XRD patterns of bulk CuO and Cs promoted CuO catalysts: (a) bulk CuO, (b) Cs/Cu = 0.05, (c) Cs/Cu = 0.1, (d) Cs/Cu = 0.15, (e) Cs/Cu = 0.2, (*) CuO, (#) Cs₂O₃**Fig. 2** TPR profile of bulk CuO and Cs promoted CuO catalysts: (a) bulk CuO, (b) Cs/Cu = 0.05, (c) Cs/Cu = 0.1, (d) Cs/Cu = 0.15, (e) Cs/Cu = 0.2

state of Cu. A similar type of trend has been reported, which is an indication of electronic promoting function of Cs to Al–Cu catalysts [42]. At higher Cs content CuO

**Fig. 3** XPS patterns of bulk CuO and Cs promoted CuO catalysts: (a) bulk CuO, (b) Cs/Cu = 0.05, (c) Cs/Cu = 0.1, (d) Cs/Cu = 0.15, (e) Cs/Cu = 0.2

reduction peaks were shifted to higher temperatures. It is known that at high concentrations of Cs it migrate to Cu surface leading to reduction inhibiting counter effect [43].

XPS measurements were performed to examine the influence of alkali metals on the surface electronic state of CuO. Figure 3 shows the XPS spectra of Cs/CuO with different Cs/Cu atomic ratios in the Cu 2p region. The peak of Cu 2p_{3/2} binding energy for all the samples appeared at around 934.2–934.6 eV. The Cu 2p_{3/2} binding energies for bulk CuO and Cs/Cu catalyst ratio with 0.1 are showed at 934.6 and 934.2 eV, respectively. The addition of Cs–CuO leads to a slight shift in BE of the Cu 2p_{3/2} to a lower value [44] is noticed. It is well known that electron donation from alkali metal to transition metals causes a change in the

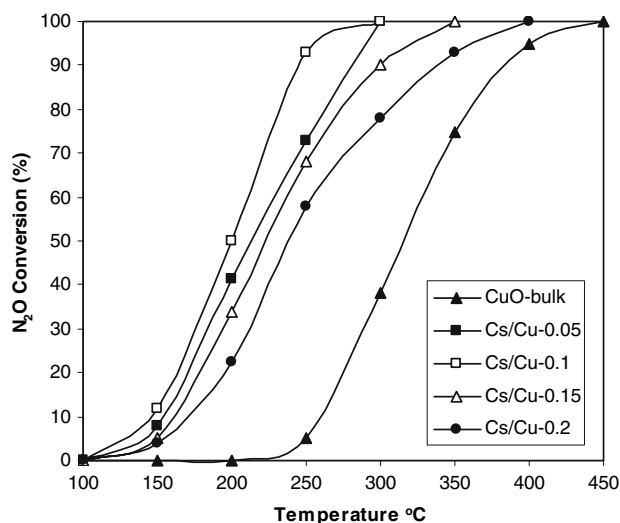


Fig. 4 N_2O activity of bulk Co_3O_4 and Cs promoted Co_3O_4 catalysts: ($\blacktriangle$) CuO bulk, ($\blacksquare$) Cs/Cu = 0.05, ($\square$) Cs/Cu = 0.1, ($\triangle$) Cs/Cu = 0.15, ($\bullet$) Cs/Cu = 0.2

electronic state of Cu. A similar type of shift in the BE value has been reported for K promoted Co_3O_4 catalyst [45]. The reduction in BE values indicates a change in the electronic state of Cu which means that the Cu–O bond is weakened with the addition of Cs. No further shift in the BE of Cu $2p_{3/2}$ observed, when Cs/Cu atomic ratio is increased further. In agreement with this, the BE for Cs $3d_{3/2}$ did not change for any of the Cs promoted CuO catalysts.

The activity profiles of the catalysts for the decomposition of N_2O are shown in Fig. 4. On the bulk CuO catalysts, the decomposition of N_2O started at 250 °C and the complete conversion occurred at 400 °C, whereas on the Cs promoted catalysts particularly with Cs/Cu ratio 0.05 and 0.1 attained 100% conversion of N_2O at 300 °C itself. The presence of small amount of Cs monotonically increased the N_2O decomposition at lower temperatures. Further increase in Cs content (Cs/Cu ratio above 0.15) leads to decrease in the N_2O decomposition activity.

To understand the influence of Cs on CuO in enhancing the N_2O decomposition activity, the bulk CuO and the Cs promoted CuO catalysts with Cs/Cu ratio of 0.1 are studied for the temperature programmed desorption of N_2O . Figure 5 shows the temperature programmed desorption profiles of N_2O adsorbed on CuO and Cs doped CuO (Cs/Cu = 0.1). The bulk CuO sample shows the desorption peak of O_2 at a temperature of 420 °C and the Cs doped CuO samples show the O_2 desorption peak at 340 °C. The desorption of N_2 is occurred in three stages in the temperature range of 260–600 °C for bulk CuO and 160–550 °C for Cs promoted CuO catalysts. 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

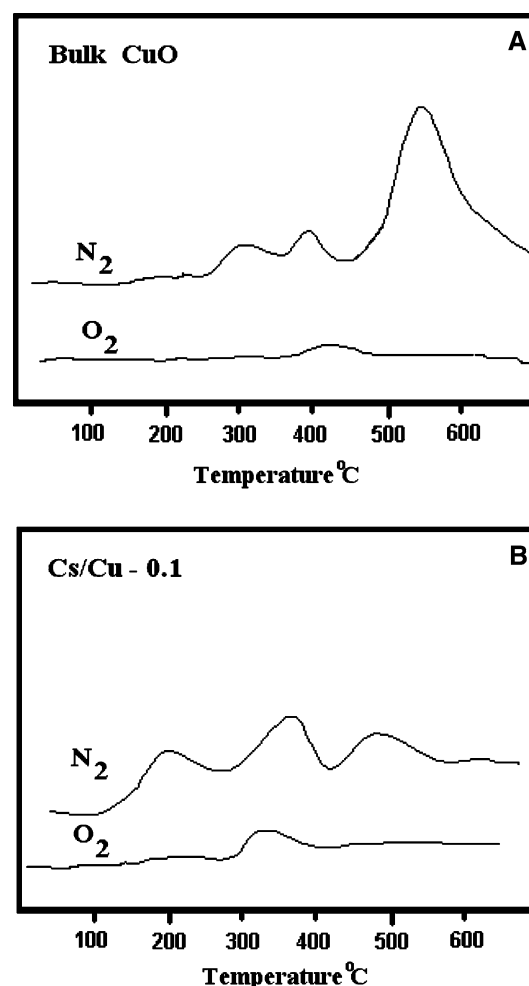


Fig. 5 N_2O -TPD profiles of (a) bulk CuO, (b) Cs/Cu = 0.1 catalysts

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 known [46]. It is apparent that the temperatures of O_2 and N_2 desorption were significantly shifted to lower values for the Cs containing CuO catalyst. The TPR result shows the early reduction of Cs promoted CuO catalyst when compare to bulk CuO. XPS results also suggest a change in electronic state of Cu with addition of small amount of Cs. The N_2O decomposition activity and the deactivation of the catalysts depend on the ability of oxygen release from the surface. Generally, the catalysts for this reaction are readily deactivated by the strong adsorption of O_2 . The early desorption of O_2 in case of Cs promoted catalysts might be the reason for its high activity at low reaction temperatures.

Stability of the CuO and Cs promoted CuO catalyst for N_2O decomposition was examined at 400 and 300 °C respectively, and the results are shown in Fig. 6. The Cs promoted catalyst maintained >90% N_2O conversion for the period study i.e., 12 h. It is noteworthy that the Cs

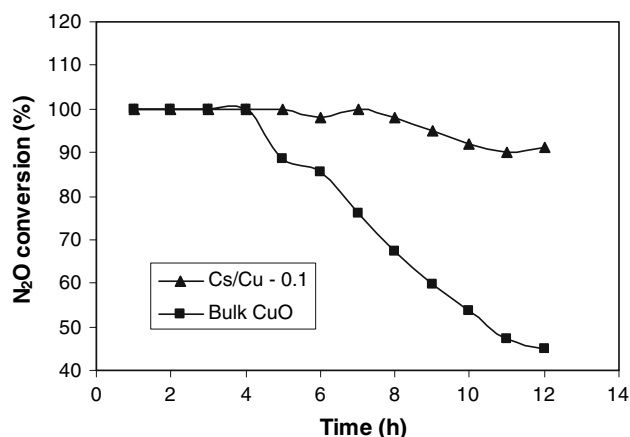


Fig. 6 Time on stream analysis on bulk CuO and Cs promoted CuO (Cs/Cu = 0.1) catalysts: (■) bulk CuO, (▲) Cs/Cu = 0.1 catalysts

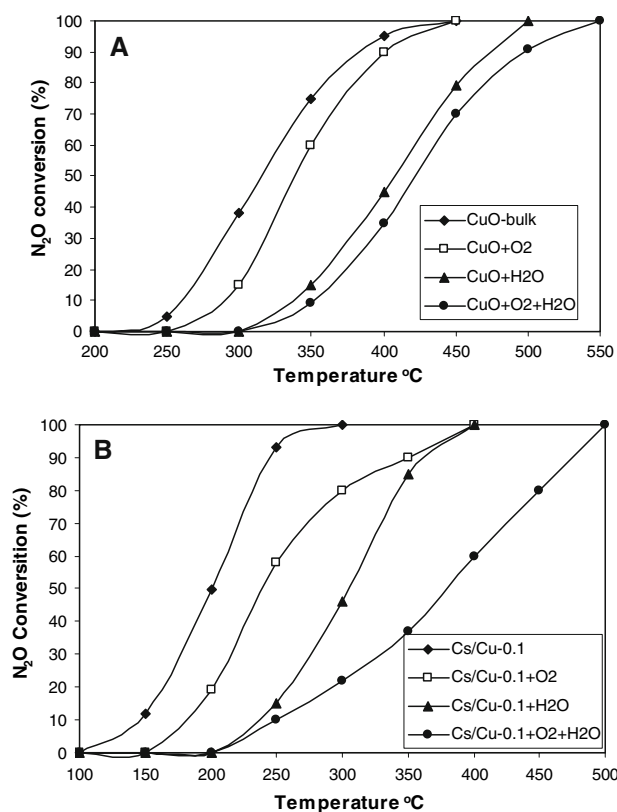


Fig. 7 N₂O decomposition to N₂ and O₂ over (a) bulk CuO and (b) Cs/Cu = 0.1 catalysts at different feed compositions: (■) 2,500 ppm N₂O, (□) 2,500 ppm N₂O + 4% O₂, (▲) 2,500 ppm N₂O + 2% H₂O, and (●) 2,500 ppm N₂O + 4% O₂ + 2% H₂O

promoted catalyst exhibited a stable activity during the entire time of operation. However, the bulk CuO catalyst has started deactivating with in 3 h of operation. This might be due to the accumulation of oxygen on the surface of CuO. It is well known that noble metal catalysts have quite highly activity for decomposition of N₂O, more over

Rh catalyst was reported to catalyze the reaction even at room temperature [47]. However, oxygen atoms formed by the decomposition of N₂O were accumulated on the Rh surface, and therefore, the activity of the catalyst decreased suddenly after high N₂O conversion for a while. On the contrary, the present Cs promoted CuO catalyst maintained high activity for more than 12 h. This result suggests that oxygen formed by the decomposition of N₂O is easily desorbed from the surface of the present catalyst.

The presence of excess O₂ and H₂O often inhibited the decomposition reaction of N₂O over most of the catalysts for N₂O decomposition [4, 5, 14, 48–51]. Figure 7a, b shows N₂O conversion in the presence of O₂ and H₂O over CuO and Cs promoted CuO catalysts, respectively. Although pure CuO had showed good activity for N₂O decomposition, the Cs promoted CuO led to a significant improvement in catalytic performance for N₂O decomposition, making the N₂O conversion curves to shift more than 100 °C to lower temperatures. The presence of excess O₂ and water (steam) inhibited the N₂O decomposition reaction, which suggests that molecular oxygen and water competed with N₂O to adsorb on active sites of the catalyst, thus suppressing the decomposition of N₂O. The inhibition of O₂ for N₂O decomposition over Cs promoted CuO is weaker compared to bulk CuO, indicating that the adsorption of O₂ on CuO is stronger than that on Cs promoted catalysts.

4 Conclusions

The present results demonstrate that the addition of Cs to CuO leads to an enhanced catalytic activity for the direct decomposition of N₂O. The Cs promoted CuO catalysts showed stable activity over bulk CuO catalyst. The XPS, TPR, and TPD measurements suggest that desorption of oxygen was promoted by the addition of Cs–CuO catalyst. The catalyst with Cs/Cu ratio of 0.1 exhibits the best catalytic activity even in the presence of O₂, H₂O during N₂O decomposition.

References

1. Thiemens MH, Troglér WC (1991) *Science* 251:932
2. Pérez-Ramírez J, Kapteijn F, Schöffel K, Moulijn JA (2003) *Appl Catal B* 44:117
3. Troglér WC (1999) *Coord Chem Rev* 187:303
4. Kapteijn F, Rodríguez-Mirasol J, Moulijn JA (1996) *Appl Catal B Environ* 9:25
5. Centi G, Galli A, Montanari B, Perathoner S, Vaccari A (1997) *Catal Today* 35:113
6. Yuzaki K, Yarimizu T, Aoyagi K, Ito S, Kunimori K (1998) *Catal Today* 45:129
7. Haber J, Machej T, Janas J, Nattich M (2004) *Catal Today* 90:15

8. Satsuma A, Maeshima H, Watanabe K, Suzuki K, Hattori T (2000) *Catal Today* 63:347
9. Drago R, Jurczyk K, Kob N (1997) *Appl Catal B Environ* 13:69
10. Kannan S, Swamy CS (1999) *Catal Today* 53:725
11. Armor JN, Braymer TA, Farris TS, Li Y, Petrocelli FP, Weist EL, Kannan S, Swamy CS (1996) *Appl Catal B* 7:397
12. Chellam U, Xu ZP, Zeng HC (2000) *Chem Mater* 12:650
13. Pieterse J, Booneveld S, Brink R (2004) *Appl Catal B Environ* 51:215
14. Perez-Ramirez J, Kapteijin F, Mul G, Moulijn JA (2001) *Chem Commun* 8:693
15. da Cruz RS, Mascarenhas AJS, Andrade HMC (1998) *Appl Catal B Environ* 18:223
16. Tzitzios VK, Georgakilas V (2005) *Chemosphere* 59:887
17. Praliaud H, Mikhailenko S, Chajar Z, Primet M (1998) *Appl Catal B* 16:359
18. Radtke F, Koepfel RA, Minardi EG, Baiker A (1997) *J Catal* 167:127
19. Agrell J, Birgersson H, Boutonnet M, Melian-Cabrera I, Navarro RM, Fierro JLG (2003) *J Catal* 219:389
20. Kim TW, Song MW, Koh HL, Kim KL (2001) *Appl Catal A* 210:35
21. Ma Z-Y, Yang C, Wei W, Li W-H, Sun Y-H (2005) *J Mol Catal A* 23:75
22. Saadi A, Rassoul Z, Bettahar MM (2000) *J Mol Catal A* 164:205
23. Rao R, Dandekar A, Baker RTK, Vannice MA (1997) *J Catal* 171:406
24. Chary KVR, Sagar GV, Naresh D, Seela KK, Sreedhar B (2005) *J Phys Chem B* 109:9437
25. Fabina MT, Schmal M (1997) *Appl Catal A* 163:153
26. Fridman VZ, Davydov AA (2000) *J Catal* 195:20
27. Liu Z, Amiridis MD, Chen Y (2005) *J Phys Chem B* 109:1251
28. Tuti S, Pepe F, Pietrogiamici D, Indovina V (2001) *React Kinet Catal Lett* 72:35
29. Yao K-W, Jaenicke S, Lin J-Y, Tan KL (1998) *Appl Catal B Environ* 16:291
30. Bennici S, Gervasini A (2006) *Appl Catal B Environ* 62:336
31. Ma J, Rodriguez NM, Vannice MA, Baker RTK (2000) *Top Catal* 10:27
32. Boissel V, Tahir S, Ann Koh C (2006) *Appl Catal B Environ* 64:234
33. Ohnishi C, Asano K, Iwamoto S, Chikama K, Inoue M (2007) *Catal Today* 120:145
34. Satsuma A, Maeshima H, Watanabe K, Hattori T (2001) *Energ Convers Manage* 42:1997
35. Alini S, Basile F, Blasioli S, Rinaldi C, Vaccari A (2007) *Appl Catal B Environ* 70:323
36. Turek T (1996) *Appl Catal B Environ* 9:201
37. Dandekar A, Vannice MA (1999) *Appl Catal B Environ* 22:179
38. Chang S-S, Lee H-J, Park HJ (2005) *Ceram Int* 31:411
39. Batista J, Pintar A, Mandrino D, Jenko M, Martin V (2001) *Appl Catal A* 206:113
40. Gentry SJ, Hurst NW, Jones A (1981) *J Chem Soc Faraday Trans* 177:603
41. Torre-Abreu C, Ribeiro MF, Henriques C, Delahay G (1997) *Appl Catal B* 14:261
42. de Auino AD, Cobo AJG (2001) *Catal Today* 65:209
43. Aika K-I, Hori H, Ozaki A (1972) *J Catal* 27:424
44. Chaturvedi S, Rodriguez JA, Hrbek J (1997) *Surf Sci* 384:260
45. Haneda M, Kintaichi Y, Bion N, Hamada H (2003) *Appl Catal B Environ* 46:473
46. Fanson PT, Stradt MW, Delgass WN, Lauterbach J (2001) *Catal Lett* 77:15
47. Centi G, Dall'Olio L, Perathoner S (2000) *Catal Lett* 67:107
48. Yan L, Ren T, Wang X, Ji D, Suo J (2003) *Appl Catal B Environ* 45:85
49. Kapteijn F, Marban G, Rodriguez-Mirasol J, Moulijn JA (1997) *J Catal* 167:256
50. Yuzaki K, Yarimizu T, Ito S-I, Kunimori K (1997) *Catal Lett* 47:173
51. Chang Y-F, McCarty JG, Wachsman ED (1995) *Appl Catal B* 6:21