Low-temperature CO Oxidation over Coprecipitated Co–Ce–Mn Oxides

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Co_3O_4–CeO_2–MnO_x catalysts prepared by coprecipitation are very active for CO oxidation at low temperature, and 100% CO conversion is obtained at −70 °C over the best catalyst; Adding a small mount of MnO_x in CoO_x–CeO_2 can improve the dispersion of cobalt oxide and ceria effectively, which leads to high CO oxidation activity.

The low-temperature catalytic oxidation of CO is of considerable concern owing to its many application fields such as environmental pollution control.[1] This reaction has also been extensively studied as a probe reaction for the oxidation mechanism in catalysis. Noble and transition metals such as Pt, Au, and Cu based catalysts have been widely investigated for low-temperature CO oxidation.[2] However, only nano-gold catalysts exhibit high activity for CO oxidation below room temperature.

CoO_x/CeO_2 catalysts were reported to be very active for CO oxidation.[3] In the present work, it is found that MnO_x-modified Co_3O_4–CeO_2 catalysts exhibit very good activity for CO oxidation at around −80 °C, and the activity is much higher than Co_3O_4/CeO_2.

Co_3O_4–CeO_2–MnO_x catalysts were prepared by a coprecipitation method. Aqueous solutions of $Ce(NO_3)_3$, $Co(NO_3)_2$, and $Mn(NO_3)_2$ were mixed at desired ratios. Then this solution and a sodium carbonate solution were gradually and simultaneously added into a continuously stirred flask, maintaining the pH of the solution within the range of 8.5–9.5. After an aging period of 4 h, the resultant precipitates were filtered and washed with hot water several times. Then they were dried at 80 °C for 24 h and calcined at 350 °C for 5 h. The so-prepared catalysts were denoted as *a*Co–*b*Ce–*c*Mn, in which *a*, *b*, and *c* represented the molar ratio of Co, Ce, and Mn.

Transmission electron microscopy (TEM) analysis was performed using a Philips G2 F-20 microscope equipped with an energy-dispersive X-ray (EDX) instrument.

The catalytic activity tests were carried out in a fixed bed flow reactor system under atmospheric pressure at a space velocity of $20000\,mL\cdot h^{-1}\cdot g_{cat}{}^{-1}$. Before the measurements, catalysts were oxidized with the gas mixture of 5 vol % O_2/N_2 at 300 °C for 40 min. The reactor was cooled to the reaction temperature before introducing the reactant. The reaction gas mixture was composed of air and a mixture of CO/N_2, containing 1 vol % CO, 19 vol % O_2 and N_2 balance. The influence of H_2O on CO oxidation was examined by adding 3.6 vol % H_2O into the feeding gases. The reactant had no pretreatment before introducing it into the reactor. After a running time of 20 min at each reaction temperature, the outlet gas mixtures from the reactor were analyzed with a gas chromatograph system (GC) equipped with TCD and FID detectors. In order to make sure it was the catalytic conversion of CO to CO_2, both CO and CO_2 in the effluence gas were detected by GC equipped with 5A molecular sieve column and GDX column. For enhancing the precision of the detection, CO and CO_2 in the outlet gas mixtures were converted to CH_4 by a nickel catalytic converter. Thus, the limit of CO and CO_2 detection was below 10 ppm.

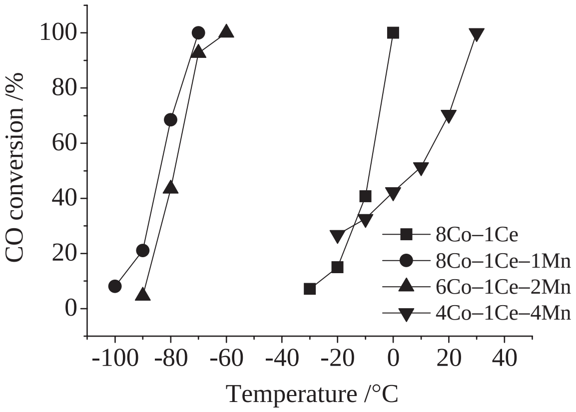

Figure 1. Variation of CO conversion with reaction temperature over 8Co–1Ce, 8Co–1Ce–1Mn, 6Co–1Ce–2Mn, and 4Co–1Ce–4Mn catalysts.

Figure 1 shows the catalytic activity of 8Co–1Ce and Co–Ce–Mn catalysts with different molar ratios for CO oxidation. As can be observed in Figure 1, adding a small amount of MnO_x dramatically promotes the catalytic activity of 8Co–1Ce, while the activity drops with further increasing the proportion of MnO_x. Over 8Co–1Ce–1Mn catalyst, obvious CO conversion is detected at −100 °C, and full CO conversion can be obtained at about −70 °C.

The CO oxidation activity at such low temperature over metal or metal oxide catalysts has been rarely reported, except for nano-gold catalysts which exhibit the best activity for low-temperature CO oxidation so far.

During the 14th International Congress on Catalysis (July, 2008), two reports on Co_3O_4 catalysts for low-temperature CO oxidation were presented. Shen and co-workers[4] found that nano cobalt oxide rods could catalyze CO oxidation at −77 °C. Yu et al.[5] reported that nano Co_3O_4 exhibited good activity for CO oxidation at around −80 °C. In this work, we find that the mixed oxide of 8Co–1Ce–1Mn exhibits similar CO oxidation activity.

Figure 2 shows the influence of H_2O on CO oxidation over 8Co–1Ce and 8Co–1Ce–1Mn samples. Adding water into the feeding streams leads to a significant decrease of CO conversion over both 8Co–1Ce–1Mn and 8Co–1Ce catalysts.

Figure 3 presents TEM images of 8Co–1Ce and 8Co–1Ce–1Mn samples. From Figures 3A and 3B, it can be observed that the crystal sizes of Co_3O_4 in 8Co–1Ce are between 10 and 15 nm, consistent with the calculated results from XRD measurements.[6] Comparing Figure 3B with Figure 3C, it is seen that

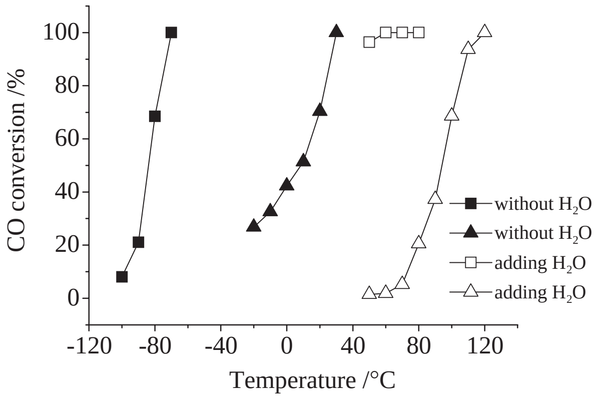

Figure 2. Influence of H_2O in the feeding gases on CO conversion over 8Co–1Ce (▲) and (△) and 8Co–1Ce–1Mn catalyst (■) and (□).

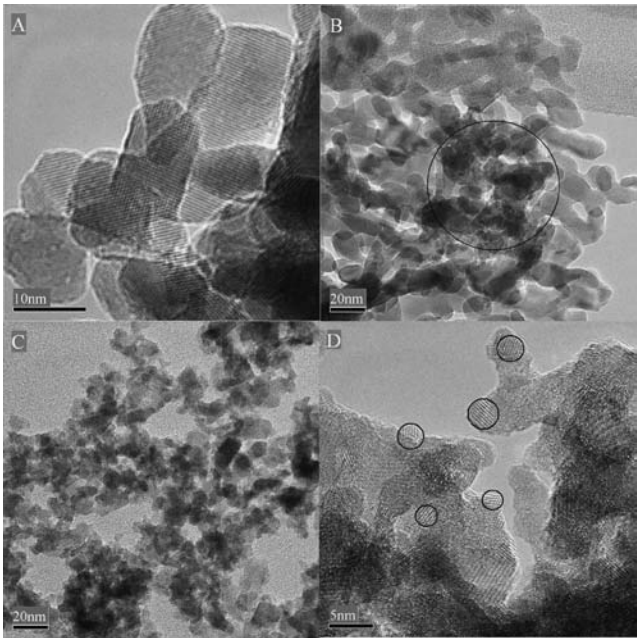

Figure 3. TEM micrographs of 8Co–1Ce catalyst (A and B) and 8Co–1Ce–1Mn catalyst (C and D).

adding MnO_x into 8Co–1Ce sample leads to an obvious decrease of Co_3O_4 crystal size, consistent with XRD results.

For a typical TEM image of 8Co–1Ce oxide (Figure 3B), the EDX results indicate that CeO_2 particles congregate inside the black circle of Figure 3B and no cerium could be detected outside the circle.[6] This suggests that Co_3O_4 and CeO_2 particles are not mixed uniformly and that a large part of Co_3O_4 particles congregate themselves and have no contact with ceria. Therefore, although ceria is beneficial for improving the dispersion of Co_3O_4 and for decreasing the particles size of Co_3O_4,[3] CeO_2 and Co_3O_4 are not well mixed in the Co_3O_4–CeO_2 sample, and a large portion of cobalt oxide has no interaction with ceria accordingly. With the addition of MnO_x, the dispersion of Co_3O_4 and CeO_2 is largely improved, as shown in Figures 3C and 3D. In the black circles of Figure 3D, nanocrystalline CeO_2 particles, which can be distinguished by the typical space distance between crystal face of ceria, are dispersed evenly. Thus Co_3O_4 particles can intimately contact ceria.

Pure Co_3O_4 has been found to show high activity for CO oxidation at low temperature.[4,5] Separate experimental results have shown that MnO_x, CeO_2, and 1Ce–1Mn and Co–Ce–Mn mixed oxides with high Mn or Ce proportion are much less active for CO oxidation. So it is proposed that the high activity of Co–Ce–Mn oxide catalysts should be ascribed to Co_3O_4 as the active component.

Kang et al.[3] found that CoO_x/CeO_2 catalysts prepared by coprecipitation exhibited good activity for CO oxidation at about 150 °C, and they attributed the high activity to the interaction between CoO_x and CeO_2 which resulted in finely dispersed CoO_x and higher Co^{3+}/Co^{2+} ratio. Shen et al.[4] suggested that the Co^{3+} species in Co_3O_4 and the high dispersed Co_3O_4 in Co_3O_4/CeO_2 should be responsible for the high CO oxidation activity at low temperature. In this work, we find that with adding MnO_x to 8Co–1Ce sample, the congregated Co_3O_4 particles are replaced by finely dispersed Co_3O_4 which are in compact contact with ceria. Thus the interaction between Co_3O_4 and CeO_2 is enhanced significantly, which leads to higher Co^{3+}/Co^{2+} ratio (confirmed by XPS[6] and TPR, not shown here). Therefore, it is proposed that the high activity of Co–Ce–Mn catalysts for CO oxidation at low temperature should be attributed to the highly dispersed Co_3O_4 particles which interact with CeO_2. The promoting effect of MnO_x on the activity of Co_3O_4–CeO_2 is due to the fact that MnO_x largely improves the dispersion of ceria and Co_3O_4, which results in the enhancement of the interaction between Co_3O_4 and CeO_2 accordingly.

References and Notes

1 S. T. Hong, M. Matsuoka, M. Anpo, *Catal. Lett.* **2006**, *107*, 173.

2 a) L. B. Ortiz-Soto, O. S. Alexeev, M. D. Amiridis, *Langmuir* **2006**, *22*, 3112. b) D. A. Bulushev, L. Kiwi-Minsker, I. Yuranov, E. I. Suvorova, P. A. Buffat, A. Renken, *J. Catal.* **2002**, *210*, 149. c) X.-Y. Wang, S.-P. Wang, S.-R. Wang, Y.-Q. Zhao, J. Huang, S.-M. Zhang, W.-P. Huang, S.-H. Wu, *Catal. Lett.* **2006**, *112*, 115. d) H. Lian, M. Jia, W. Pan, Y. Li, W. Zhang, D. Jiang, *Catal. Commun.* **2005**, *6*, 47. e) A. C. Gluhoi, X. Tang, P. Marginean, B. E. Nieuwenhuys, *Top. Catal.* **2006**, *39*, 101. f) M. Okumura, M. Haruta, *Chem. Lett.* **2000**, 396. g) Y. Yuan, K. Asakura, H. Wan, K. Tsai, Y. Iwasawa, *Chem. Lett.* **1996**, 755. h) M.-F. Luo, J.-M. Ma, J.-Q. Lu, Y.-P. Song, Y.-J. Wang, *J. Catal.* **2007**, *246*, 52. i) X. Zheng, X. Zhang, X. Wang, S. Wang, S. Wu, *Appl. Catal., A* **2005**, *295*, 142.

3 a) M. Kang, M. W. Song, C. H. Lee, *Appl. Catal., A* **2003**, *251*, 143. b) J. Shao, P. Zhang, X. Tang, B. Zhang, W. Song, Y. Yu, W. Shen, *Chin. J. Catal.* **2007**, *28*, 163.

4 X. W. Xie, Y. Li, W. J. Shen, Abstracts of the 14th International Congress on Catalysis, 309.

5 Y. Yu, T. Takei, M. Haruta, Abstracts of the 14th International Congress on Catalysis, 466.

6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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