Catalytic oxidation of NO over MnOx-CoOx/TiO₂ in presence of low ratio of O₃/NO: the activity and

mechanism

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1 Experimental system



Fig. S1. Schematic diagram of experimental system for NO oxidation.

1-NO 2-SO₂ 3-N₂ 4-O₂ 5-MFC 6-Ozone generator 7-Ozone Detector 8-Rotameter 9-Mixer

10-Reactor 11-catalyst 12-Flue gas analyzer



2 NO oxidation properties

Fig. S2. NO conversion of 7%MnOx-CoOx/TiO2 with different molar ratio of Mn to Co. Reaction

condition: Flow=400 ml/min, NO=500 ppm, O₂=4%, GHSV=24000 h⁻¹.

Fig. S2 shows the NO conversion by using 7%MnOx-CoOx/TiO2 with different molar ratio of Mn and Co in

presence of O₂. The conversion of NO increased with the increase of temperature, reaching the maximum at 350 °C and then decreased. With the increase of manganese content, NO conversion increased, but the NO conversion by 7%MnO_x-CoO_x(4:1)/TiO₂ was lower than by 7%MnO_x-CoO_x(2:1)/TiO₂. 7%MnO_x-CoO_x(2:1)/TiO₂ showed the highest catalytic efficiency than other molar ratios. Therefore, MnO_x-CoO_x(2:1)/TiO₂ was chosen in the following studies.

3 H₂-TPR analysis



Fig. S3. H₂-TPR comparison of single load and MnO_x-CoO_x load.

 H_2 -TPR experiments on supported single MnO_x and single CoO_x are added in supplementary material, as shown in Fig. S3. For 10%MnO_x/TiO₂ and 15%MnO_x/TiO₂, there were two obvious reduction peaks. The peaks at 369 °C and 3833 °C could be assigned to the reduction of MnO₂ to Mn₂O₃ ¹, and the peaks at 544 °C and 559 °C could be assigned to the reduction of Mn₂O₃ occurred through Mn₃O₄ to MnO ². For 10%CoO_x/TiO₂ and 15%CoO_x/TiO₂, there were also two reduction peaks. The peaks at 390 °C and 406 °C could be assigned to the reduction of Co₃O₄ to CoO, and the peaks at 503 °C and 493 °C could be assigned to the reduction of CoO to Co ³. For 10%MnO_x-CoO_x(2:1)/TiO₂, there were two reduction peaks. According to the reduction peaks of 10%MnO_x/TiO₂ and 10%CoO_x/TiO₂, the reduction peak at 332 °C contains the reduction of MnO₂ to Mn₂O₃ and Co_3O_4 to CoO, and the reduction peak at 490 °C contains the reduction of Mn_2O_3 occurred through Mn_3O_4 to MnO and the reduction of CoO to Co. Compared to $10\%MnO_x/TiO_2$ and $10\%CoO_x/TiO_2$, the reduction peak temperatures of $10\%MnO_x$ - $CoO_x(2:1)/TiO_2$ was reduced. For $15\%MnO_x$ - $CoO_x(2:1)/TiO_2$, there were obvious reduction peaks at 350 °C and 511 °C with a shoulder peak at 533 °C. According to the reduction peaks of $15\%MnO_x/TiO_2$ and $15\%CoO_x/TiO_2$, the reduction peak at 350 °C contains the reduction of MnO_2 to Mn_2O_3 and Co_3O_4 to CoO, and the reduction peak at 511 °C with a shoulder peak at 533 °C represented the reduction of Mn_2O_3 occurred through Mn_3O_4 to MnO and the reduction of CoO to Co.

References

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