Transformation of nitric oxide to molecular nitrogen with 100% selectivity on catalysts made of earth-abundant elements at relatively

low temperature

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Introduction

Transformation of poisonous nitric oxide to molecular nitrogen with 100% selectivity is significant for maintaining a friendly environment. Precious metals such as Rh are highly active for reduction of NO to N₂ with CO or H₂. From sustainability point of view, a replacement catalysts made of earth-abundant element is certainly necessary in a long term. Cobalt oxide is one of the first row transition metal oxides. Compared to other first-row transition metal oxide, it exhibits a high capability in generation of oxygen vacancies. In addition, barrier for the hopping of oxygen vacancies is much lower than other oxides. As Co cations can act as sites for adsorption of nitric oxide molecules and surface lattice oxygen for binding of CO molecules, Co₃O₄ is active for reduction of NO with CO . With the aid of ambient pressure X-ray photoelectron spectroscopy, a new phase, nonstoichiometric cobalt monoxide (CoO_{1-x}) was discovered. It exhibits 100% conversion for NO to N₂ with CO at a temperature as low as 225°C.

Materials and Methods

Cobalt oxide (Co₃O₄) nanorods were synthesized following a modified hydrothermal method ¹. The large-scale image (Figure 1a) shows Co₃O₄ has a diameter of ~6 nm with a length of ~100 nm in average. High resolution image (Figure 1b) shows the crystallization of Co₃O₄ phase, supported by XRD pattern. The measured inter-planar distance, 2.88 Å is consistent with the value of (220) reported in literature (1,2). It suggests that the preferentially exposed surface is Co₃O₄ (110). Measurements of catalytic activity and selectivity in reduction of NO with CO were performed in a micro fix-bed flow reactor. Gas chromatograph analyzed gases from this reactor under different reaction conditions. Two premixed gas cylinders were used. The mixed gas in one cylinder is 15% CO + 5% NO + 80 % Ar, the other is 15% CO + 15% NO + 70% Ar. Certain amount of catalysts was loaded into the micro reactor. In-situ surface chemistry of Co₃O₄ during catalysis was characterized with AP-XPS (Figure 2)

Results

Here we report the restructuring of pure Co_3O_4 in gaseous environments. We found that a new catalytic phase, nonstoichiometric rock-salt cobalt monoxide CoO_{1-x} , can be formed through a restructuring of Co_3O_4 nanorods under reaction conditions. The restructuring of Co_3O_4 and formation of nonstoichiometric rock-salt CoO_{1-x} under reaction conditions were monitored through in situ studies using ambient





pressure X-ray photoelectron spectroscopy (AP-XPS) (Figure 3) and environmental transmission electron microscopy (E-TEM) (Figure 4). The nonstoichiometric rock-salt CoO $_{1-x}$ is highly active in the reduction of nitric oxide (NO) with carbon monoxide (CO) for producing N₂ with 100% selectivity (Figure 5). This catalyst formed through restructuring, exhibits an activity similar to Rh-based catalysts. The 100% selectivity for production of N₂ remains constant at 520 °C for at least 96 h. In situ studies of this catalyst show that the surface of cobalt monoxide nanorods is nonstoichiometric with ~20%-25% oxygen vacancies.

Figure 2Pictures of the AP-XPS system working at Torr pressure range in the PI's group. (a) AP-XPS system. (b) Electronic control unit.



Figure 4 Diffraction pattern of Co_3O_4 at 250°C (a) and (b) 350°C and electron enery loss spectra at room temperature (25°C) (c) and 350°C (d) in a reactive environment.





Figure 3 Evolution of photoemission feature of Co 2p (a) and Co 2p3/2 (b) of Co_3O_4 in the mixture of CO and NO at different reaction temperature.



Figure 5 Catalytic activity (the left Y-axis, black line in figure) and selectivity (the right Y-axis, red line in figure) of Co_3O_4 and CoO_{1-x} .



References

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