

Restructuring Early Transition Metal Oxide for New Catalysis

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Early transition metal oxide is one main category of heterogeneous catalysts. Most of them are reducible oxides. Oxygen vacancies can be generated on surface or bulk in gaseous environment. Even a phase transformation could be performed under the reaction condition of catalysis. Both processes could happen to an early transition metal oxide during catalysis. Removal of poisonous gases, including nitric oxide and carbon monoxide, released from vehicle engines and chemical industries is critical toward a sustainable environment. The search for cost-effective catalysts without any non-precious metals highly selective and active in reduction of nitric oxide to nitrogen (N₂) has remained a significant challenge. We successfully developed a new catalyst through restructuring of a pure early transition metal oxide. Non-stoichiometric cobalt monoxide is formed from as-synthesized Co₃O₄ nanorods under reaction conditions. Rock-salt CoO_{1-x} exhibits distinctly different catalytic performance in contrast to the original Co₃O₄ of spinel phase. The active phase was identified with advanced in-situ micro analytical techniques including environmental TEM (E-TEM) and ambient pressure X-ray photoelectron spectroscopy (AP-XPS).

As shown in Figure 1 diffraction pattern of Co₃O₄ is transformed to CoO at a temperature of 250-300°C in an environment of CO. This is consistent with in-situ EELS spectra under the same reaction condition. These studies showed a transformation of bulk phase from Co₃O₄ to CoO. Evolution of surface phase under catalytic conditions (a mixture of two reactants CO and NO) was tracked with ambient pressure XPS. Figure 2a presents the photoemission feature of Co 2p and O 1s of the catalyst at different reaction temperatures. Photoemission features of Co 2p_{3/2} and Co 2p_{1/2} of Co₃O₄ nanorods were identified at 779.8 eV and 795.1 eV, consistent with those of Co₃O₄ nanoparticles and single crystals. CoO is formed from Co₃O₄ in reactant gases during catalysis. AP-XPS studies showed the Co₃O₄ is partially reduced to CoO at 250°C in a mixture of CO and NO with a ratio of partial pressures of 3:1. The reduction of Co₃O₄ to CoO is evident by the appearance of satellite peaks marked in Figure 2a9. The satellite peaks of Co 2p of CoO were identified at 786.4 eV and 803.0 eV for Co 2p_{3/2} and Co 2p_{1/2}, respectively, which are ~5.9 eV and ~6.7 eV higher than the corresponding main photoemission features at ~780.5 eV and ~796.3 eV. At 400°C-500°C, Co₃O₄ is completely reduced to CoO in CO+NO and no photoemission feature of metallic cobalt is observed.

The in-situ formed CoO catalyst is highly active for reducing NO with CO. Catalytic measurements showed the evolution of catalytic selectivity in the production of N₂ as a function of reaction temperature (Figure 2b). At 110°C, Co₃O₄ exhibits a detectable conversion of NO (17%), but only N₂O is produced. The conversion of NO at 150°C is 85% with an N₂ selectivity of 9.0%; at 170°C the conversion of NO reaches 100%. Selectivity to production of N₂ increases progressively in the temperature regime of 170°C-420°C and reaches 100% at 420°C, followed by maintaining the 100% selectivity through 480°C. Upon measurements at 480°C, the catalyst was cooled down to 300°C and then 250°C; AP-XPS studies showed the surface of the catalyst still remains at the chemical state of CoO at 250°C under this reaction conditions (Figure 2a16). Selectivity to N₂ at 300°C and 250°C is 100% (Figure 2b). The turn-over-frequency (TOF) of N₂ production at 420°C is 1.55 N₂ molecules per

cobalt atom per second, higher than 0.08-0.27 of Rh nanocatalysts. It is stable up to 36 hours at 420°C without any loss of activity and selectivity (100%). At 48th hour, selectivity to the production of N₂ is decreased to 95% though high activity still remains. In-situ studies revealed that the active phase is nonstoichiometric CoO. This work demonstrated that restructuring of early transition metal oxide can be used for development of catalysts.

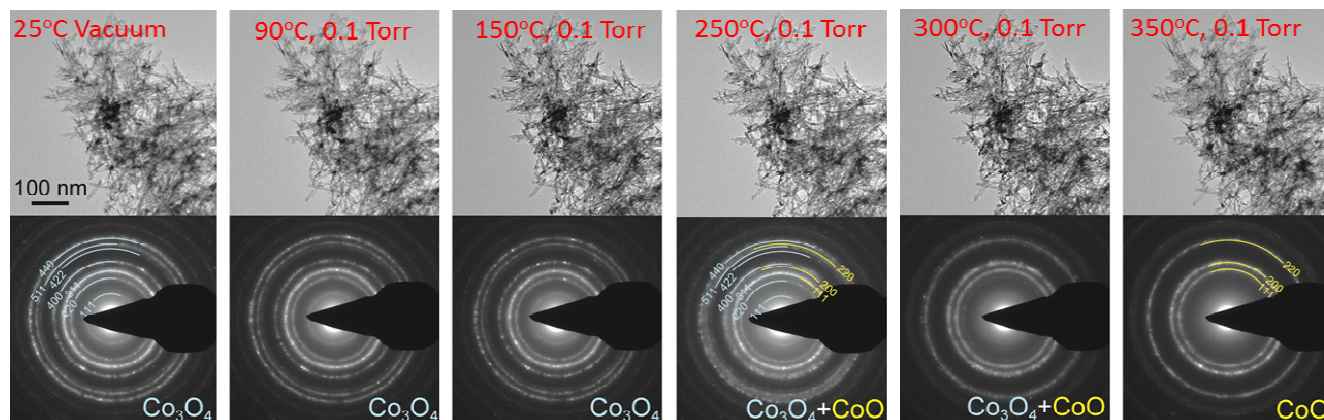


Figure 1. Diffraction patterns of as-synthesized Co₃O₄ under reaction conditions at different temperature. Images were collected with E-TEM when the catalyst was in gaseous environment.

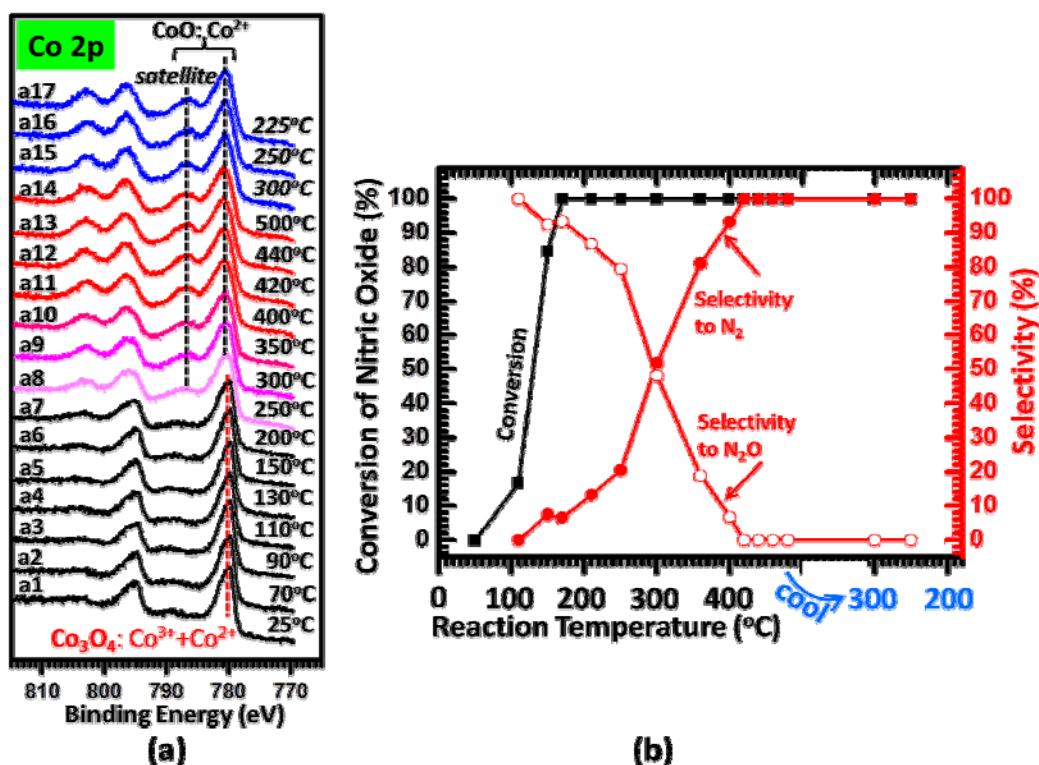


Figure 2. In-situ surface chemistry of the catalyst and the corresponding catalytic performance at different temperatures. (a) Co 2p photoemission feature of catalysts during catalysis in 3 Torr CO and 1 Torr NO studies with AP-XPS. (b) Catalytic activity (left axis) and selectivity (right axis) as a function of reaction temperature.