

# Co<sub>3</sub>O<sub>4</sub> Nanorods for Low Temperature Oxidation of Carbon Monoxide

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**Abstract:** Co<sub>3</sub>O<sub>4</sub> nanorods were found to be not only sufficiently active for CO oxidation at a temperature as low as -77°C, but also sustainably stable in a stream of normal feed gases containing moisture. The reaction rate of CO oxidation over the Co<sub>3</sub>O<sub>4</sub> nanorods with very low apparent activation energy of 22 kJ/mol was at least one order of magnitude larger than those over the conventional nanoparticles. High-resolution transmission electron microscopy observation proved that the single crystal Co<sub>3</sub>O<sub>4</sub> nanorods predominantly exposed the {110} planes that favor the presence of octahedrally coordinated Co<sup>3+</sup> species, which may act as the active sites for CO oxidation. The above results indicate a possibility of replacing noble metals with morphology-controlled base metal oxides in the currently used catalysts for automotive-emissions control, particularly, during the cold-start transient.

**Keywords:** Co<sub>3</sub>O<sub>4</sub> nanorods, CO oxidation, Low-temperature.

## 1. Introduction

Low-temperature CO oxidation is widely used in automotive-emissions control, closed-cycle COB<sub>2B</sub> lasers, gas sensors and indoor air purification. Particularly, the heavily emitted CO and hydrocarbons of automobiles during the cold-start transient requires novel catalysts to removal the emissions below 200°C.<sup>1</sup> Cobalt oxides have long been regarded as the most active catalysts for CO oxidation at low temperature, but they are very sensitive to the moisture in the feed gases and thus the activities remarkably decrease during the course of reaction.<sup>2</sup> Here, we show that Co<sub>3</sub>O<sub>4</sub> nanorods could catalyze CO oxidation with extremely high activity and sustainable stability, giving 100% CO conversion at a temperature as low as -77°C.

## 2. Experimental

The Co<sub>3</sub>O<sub>4</sub> nanorods and nanoparticles were prepared by precipitation of cobalt acetate and sodium carbonate aqueous solution with the mediation of ethylene glycol at 80-160°C, followed by calcination at 450°C in air. CO oxidation reaction was conducted in a continuous flow fixed-bed quartz reactor under atmospheric pressure at -77°C with a typical feed stream of 1% CO/2.5% O<sub>2</sub>/He. The oxidation of CO under dry condition was conducted by passing the reaction gas mixture through a molecular sieve trap cooled by dry ice to remove the traceable amounts of moisture.

## 3. Results and discussion

HRTEM observations (Fig. 1) indicated that the Co<sub>3</sub>O<sub>4</sub> nanorods had single crystal structure with a diameter of 10-20 nm and a length of 100-300 nm. This unique morphology of nanorods grew along the [110] direction and preferentially exposed the well-defined (110) plane with octahedrally coordinated CoP<sup>3+</sup> species.

As shown in Fig. 2, the Co<sub>3</sub>O<sub>4</sub> nanorods showed 100% CO conversion during the initial 6 hours time-on-stream, and then the CO conversion tended to decrease but only down to 80% after reaction for 12 hours for CO oxidation even at -77°C. When the reaction was performed under dry condition by removing traceable amounts of moisture in the feed gases, there was no remarkable difference in CO conversion during the initial 6 hours time-on-stream, and only relatively higher CO conversion was obtained than that under normal condition in the following 6 hours, suggesting that the Co<sub>3</sub>O<sub>4</sub> nanorods is not so sensitive to the presence of moisture, unlike the conventional nanoparticle. Kinetic measurements further indicated that

the specific reaction rate of CO oxidation over the  $\text{Co}_3\text{O}_4$  nanorods at  $-77^\circ\text{C}$  was  $3.91 \times 10^{-6}$  mol CO/g.s for normal feed gases, which is at  $-77^\circ\text{C}$ , which was one order of magnitude larger than that over the nanoparticles. The apparent activation energy of CO oxidation over the  $\text{Co}_3\text{O}_4$  nanorods was only 22 kJ/mol, implying that the reaction rate is less sensitive to temperature. The reaction orders of CO and  $\text{O}_2$  in CO oxidation over the nanorods were estimated to be 0.12 and 0.28, respectively. Accordingly, the preexponential factor was calculated to be  $5.7 \times 10^{26}$  molecules/g.s, which is not only very larger than the theoretical values of  $10^{14}$  to  $10^{15}$  molecules/cm<sup>3</sup>.s for a two molecule reaction, but also even larger than the values obtained over supported gold catalysts ( $1.0 \times 10^{25}$  molecules/g.s for Au/TiO<sub>2</sub> and  $1.9 \times 10^{21}$  molecules/g.s for Au/Co<sub>3</sub>O<sub>4</sub>, respectively)<sup>3</sup>. That is, the number of active sites on the  $\text{Co}_3\text{O}_4$  nanorods is sufficiently large, and the active sites might be only gradually blocked by the H<sub>2</sub>O/OH- and/or carbonates deposits during the course of reaction, unlike the conventional nanoparticles. Regeneration tests together with CO<sub>2</sub> addition to the reaction feed proved that the gradual deactivation of the nanorods during the course of reaction was mainly due to the accumulation of carbonates and H<sub>2</sub>O/OH species on the surface, but they could be easily removed by thermal treatment with oxygen-containing atmosphere. The activities could be fully recovered or even superior to their initial levels, suggesting that that the deactivation was a reversible process.

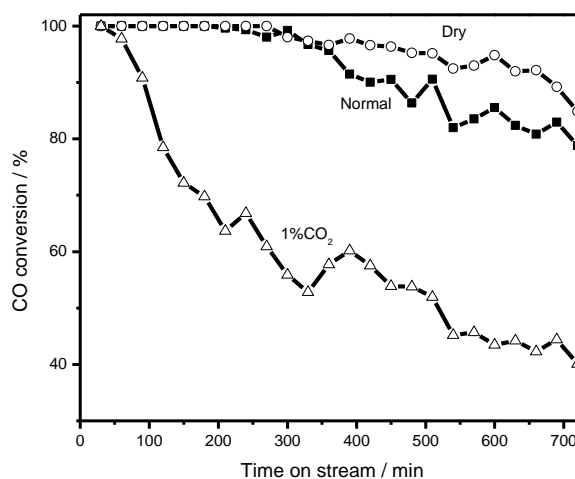
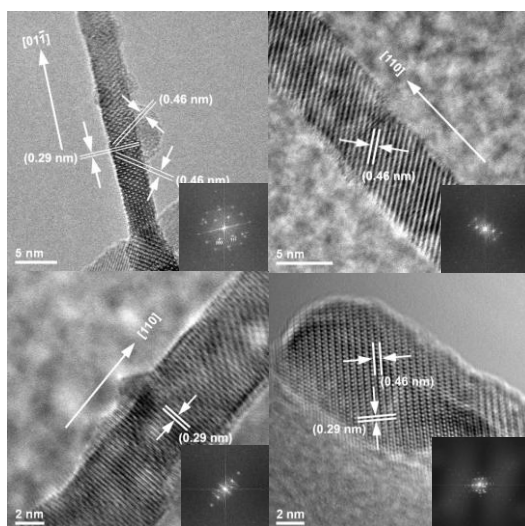


Fig. 1 HRTEM images of the  $\text{Co}_3\text{O}_4$  nanorods. Fig. 2. CO conversions over the  $\text{Co}_3\text{O}_4$  nanorods under normal and dry conditions.  $-77^\circ\text{C}$ , 200 mg catalyst, 50 ml/min.

#### 4. Conclusion

Nanorod-shaped  $\text{Co}_3\text{O}_4$  exhibits a unique morphological feature of preferentially exposing the {110} planes, which is richness in  $\text{Co}^{3+}$  sites. This novel structured catalyst shows extraordinary activity for CO oxidation, yielding 100% CO conversion at a temperature as low as at  $-77^\circ\text{C}$ , and essentially resistant to the accumulation of H<sub>2</sub>O/OH species and carbonates.

#### References

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