# The Effect of Support on NO Oxidation over Supported $Co_3O_4$ Catalysts

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## Introduction

Nitrogen oxides ($NO_x$) have been considered to be one of main pollutants to be eliminated. Among known various methodologies, the selective catalytic reduction (SCR) with various reducing agents involving $NH_3$ and hydrocarbons has been generally accepted to be most promising one. Recently, it has been reported that the co-presence of $NO_2$ with NO can accelerate the $NH_3$-SCR [1]. Furthermore, it has been frequently reported that $NO_2$ has a beneficial effect on the SCR with hydrocarbons. In the lean burning natural gas or diesel engine, $NO_x$ is mainly composed of NO. Therefore, the oxidation of NO into $NO_2$ can be an important reaction for $NO_x$ control. Until now, several catalyst systems have been examined for NO oxidation. They can be grouped into the noble metals [2] and the transition metal oxides [3] catalysts. Among noble metal catalysts, supported Pt-based catalysts have been intensively examined. Besides of its high price, the development of catalyst system based on the transition metal oxides is required to substitute Pt-based catalysts because this Pt-based catalyst has been reported to be deactivated by several causes. The decreasing NO oxidation activity was observed with concomitant phase transformation from Pt to $PtO_x$. The presence of $SO_2$ and $H_2O$ was also reported to decrease the catalytic activity via formation of sulfate on the support and decrease in Pt surface area, respectively. Until now, Co-based catalyst systems have been frequently reported to have promising catalytic activity for NO oxidation. However, few comparison works among supported cobalt oxides have been conducted systematically. In this study, cobalt oxides catalysts prepared with different cobalt precursors, supports, and cobalt contents were compared for the NO oxidation in the absence and presence of water vapor in a feed. The effect of $SO_2$ in a feed on the catalyst stability was also examined. The observed catalytic activity was tried to be correlated with the crystalline size of $Co_3O_4$ and its interaction with supports.

## Materials and Methods

All the catalysts were prepared with a wet impregnation method from an aqueous solution of cobalt acetate or cobalt nitrate. Various metal oxides such as $TiO_2$ (P-25), yttria-stabilized zirconia (YSZ), $CeO_2$, $SiO_2$, $SiO_2$-$Al_2O_3$, $CeO_2$-$ZrO_2$ and $\gamma$-alumina were purchased and utilized as a support. 1 wt% Pt/$\gamma$-$Al_2O_3$ was purchased from Aldrich and utilized as a reference catalyst. All the catalysts were calcined at 573 K in air for 1 h before a reaction.

The $N_2$ physisorption, X-ray diffraction (XRD), temperature-programmed reduction with $H_2$ ($H_2$-TPR) and NO chemisorption were conducted to characterize catalysts.

Catalytic activities were measured over a fixed bed of catalysts in a tubular flow reactor of 8-mm i.d. Reactant gases were fed to the reactor by means of electronic mass flow controller (MKS). The reactant gas typically consisted of 500 ppm NO and 5 vol% $O_2$ in $N_2$. The NOx concentration in the inlet and outlet gas was analyzed by means of a NO/$NO_2$ combustion gas analyzer (Euroton).

## Results and Discussion

As shown in Table 1, the catalytic activity for NO oxidation at kinetically-controlled reaction temperatures decreased in the following order: Co/$CeO_2$ ~ 1 wt% Pt/$\gamma$-$Al_2O_3$ >> $Co_3O_4$ > Co/$SiO_2$ > Co/YSZ ~ Co/$CeO_2$-$ZrO_2$ > Co/$ZrO_2$ > Co/$TiO_2$ > Co/$\gamma$-$Al_2O_3$ >> Co/$SiO_2$-$Al_2O_3$. The cobalt oxides supported on the reducible metal oxides exhibited the higher catalytic activity compared with those supported on the irreducible metal oxides except Co/$SiO_2$. The most active catalyst, Co/$CeO_2$, has a comparable activity for this reaction over all reaction temperatures with a well-known noble metal catalyst, Pt/$\gamma$-$Al_2O_3$. The Co/$CeO_2$ shows the largest NO uptake which is larger than any other supported catalysts by at least 7 times. No detectable No uptake can be obtained for $CeO_2$. Therefore, the NO chemisorption can be regarded to be due to the presence of $Co_3O_4$ in the catalyst. The crystalline size of $Co_3O_4$ and the presence of the easily reducible $Co_3O_4$ during $H_2$-TPR appeared to be closely related to the low-temperature catalytic activity. The reversible and irreversible deactivation was observed over $Co_3O_4$/$CeO_2$ in the presence of water vapor and $SO_2$ in a feed, respectively. However, this deactivation due to the presence of $SO_2$ can be significantly suppressed as long as the concentration of $SO_2$ is below 10 ppm.

**Table 1.** The physicochemical properties of 10 wt% Co/supports and their catalytic activities at 553 K.

| Catalysts | Surface area [ $m^2$/g ] | Crystalline size of $Co_3O_4$ [a] [ nm ] | NO uptake at 298K [ $\mu$mol/$g_{cat.}$ ] | NO Conversion [b] [%] |
|---|---|---|---|---|
| Co/$CeO_2$ | 230 | - | 461.5 | 73.1 |
| Co/$ZrO_2$ | 86 | 10.6 | 50.2 | 32.3 |
| Co/$CeO_2$-$ZrO_2$ | 101 | 9.3 | 28.7 | 39.4 |
| Co/YSZ | 9 | 14.6 | 2.1 | 44.5 |
| Co/$\gamma$-$Al_2O_3$ | 227 | 3.0 | 23.8 | 14.9 |
| Co/$TiO_2$ | 57 | 11.6 | 11.3 | 24.8 |
| Co/$SiO_2$-$Al_2O_3$ | 430 | - | 25.9 | 6.6 |
| Co/$SiO_2$ | 272 | - | 59.9 | 56.5 |
| $Co_3O_4$ | 65 | 19.3 | 183.0 | 66.6 |

[a] Crystalline size was determined from the Scherrer line broadening equation.
[b] Reactants: 500 ppm NO, 5 % $O_2$ in $N_2$. F/W = 80 L/h/$g_{cat.}$.

## Significance

The crystalline size of $Co_3O_4$ and the presence of the easily reducible $Co_3O_4$ during $H_2$-TPR appeared to be closely related to the low-temperature catalytic activity for NO oxidation over supported cobalt oxides catalysts.

## References

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