

# Fluorine poisoning of Metal Oxide Additives on Nickel-Cobalt Catalysts for direct decomposition of N<sub>2</sub>O

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## Abstract

The decomposition of N<sub>2</sub>O to N<sub>2</sub> and O<sub>2</sub> in presence of fluorine has been studied over a series of Ni-Co catalysts modified with alkaline-earth oxide (Mg, Ca, Ba) and transition metal (Ti, Fe, Mn). The results indicate that both the stability and activity of catalysts can be improved by adding promoter. The degree of deactivity would be in the following order:

Ni-Co-Mg < Ni-Co-Ca < Ni-Co-Ba < Ni-Co-Mn < Ni-Co-Fe < Ni-Co < Ni-Co-Ti

The present study revealed that MgO is an excellent promoter for increasing both the stability and activity of Ni-Co catalyst. Two important roles of MgO have been assessed: (i) The MgO promoter well-dispersed Ni-Co particles is surrounded by fine MgO particles with a certain degree of interaction, so the formation of larger bulk Ni-Co crystallites may be reduced that improve the activity sites; (ii) The Manganese has more affinity to fluorine, so the deactivation of Ni-Co-Mg doesn't exhibited after 12 hrs of exposure to 600 ppmv HF at 400°C.

Keywords: N<sub>2</sub>O decomposition; fluorine poisoning; promoter

## 1 Introduction

Nitrous oxide (N<sub>2</sub>O) contributes to the greenhouse-effect, a phenomenon caused by strong absorbance of infrared radiation in the atmosphere. The global warming potential (GWP) per molecule of N<sub>2</sub>O is about 310 times as high as that of carbon dioxide (Rodhe, 1900). As reported by IPCC, anthropogenic N<sub>2</sub>O emissions contribute about 6% to the global greenhouse effect and 6% to the ozone layer

depletion (Houghton, 2001). In the past decade, the use of N<sub>2</sub>O has increased dramatically. This is primarily due to the development of N<sub>2</sub>O as a CVD process agent in the semiconductor industry.

Catalytic decomposition could be considered as the simplest method of N<sub>2</sub>O removal because it does not need any other chemical compound. To control the emission of N<sub>2</sub>O, many catalysts have been reported for the catalytic decomposition of N<sub>2</sub>O, including supported metals (Doi et al., 2001), pure and mixed oxides (Satsuma et al., 2000; Kannan and Swamy, 1999; Armor et al., 1996; Yan et al., 2003a,b) and zeolites (Ramírez et al., 2002,2003; Kapteijn et al., 1996). Among them, mixed oxides containing cobalt spinel showed the best catalytic activity in the decomposition of N<sub>2</sub>O (Armor et al., 1996; Yan et al., 2003a,b; Kannan and Swamy, 1999). The reaction of N<sub>2</sub>O with the catalysts is generally considered as a charge donation from the catalyst into the antibonding orbital of N<sub>2</sub>O, weakening the N-O bond and leading to scission (Kapteijn et al., 1999). A transition metal oxide like Co<sub>3</sub>O<sub>4</sub> is active for the decomposition of N<sub>2</sub>O because of its relatively high redox property.

In previous work (Yan et al., 2003a) had considered Ni as an alternative, achieving a considerable increase in the catalytic activity with respect to the Co-based mixed oxide. In addition, the decomposition of N<sub>2</sub>O catalyst compositions has failed to become practical because of their low resistance to fluorine, present in relatively high concentrations in semiconductor manufacturing process. Therefore, in this report, the possible protecting role of various metal oxides (Mg, Ca, Ba, Ti, Fe, Mn) against fluorine poisoning of Ni-Co-M catalysts is investigated to

elucidate the effects of additives on the activities and stabilities for direct decomposition of N<sub>2</sub>O reaction.

## 2 Experimental

### Catalyst Preparation

The catalysts were prepared by co-precipitation method. An aqueous solution of 1 M Na<sub>2</sub>CO<sub>3</sub> was added to a mixed aqueous solution containing known amounts of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O or M(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (M= Ba, Mg, Ca, Fe, Mn, TiCl<sub>4</sub> is used as Ti precursor) at room temperature until the pH of the solution reached 9. The resultant precipitated was washed until the filtrate was neutral, then dried at 100 °C overnight, followed by calcinations at 400°C in air for 2 h.

### Catalyst activity measurements

The catalytic reaction system (Fig. 1) was carried out in a standard fixed-bed flow reactor by passing a gaseous mixture of N<sub>2</sub>O (5%) and HF (600ppm) in a N<sub>2</sub> flow rate 40 ml/min to get a WHSV of 45 ml/mg · h. The 5% N<sub>2</sub>O gas supplied from a high-pressure gas cylinder was introduced to the 14.6% HF solution to carry the 2.5% H<sub>2</sub>O and 600 ppm HF vapor (Brosheer et al., 1947) at 25°C. To get reliable N<sub>2</sub>O conversion, the reaction system was kept for 30 min at each reaction temperature, then started to analyze the off-gases with on-line gas chromatographs GC, China Chromatograph 9800) equipped with Porapak Q columns and TCD detectors, respectively.

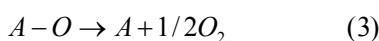
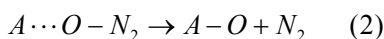
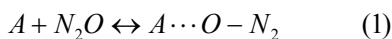
The N<sub>2</sub>O conversion is defined as follows:

$$\text{N}_2\text{O Conversion} = \frac{\text{moles of N}_2\text{O consumed}}{\text{moles of N}_2\text{O fed}}$$

## 3 Results and Discussion

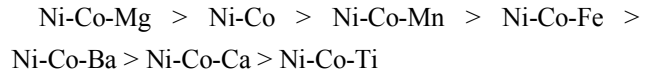
### Catalytic decomposition of N<sub>2</sub>O

The mechanistic interpretations emphasize the need for labile surface oxygen to complete the catalytic cycle by recombining, desorbing as O<sub>2</sub> and regenerating the active sites, thus maintaining a steady rate of decomposition. Based on the chemistry associated with N<sub>2</sub>O decomposition, the following generic mechanism is proposed (Kapteijn et al., 1999):



where A stands for an active site on the surface.

The decomposition of N<sub>2</sub>O tests performed after exposure to 600 ppmv HF and 2.5% H<sub>2</sub>O at 400°C during 12 hours is shown in Fig. 2. It was observed the most active catalyst is Ni-Co-Mg, the N<sub>2</sub>O conversion increased 31 % than the virgin catalyst from 46.4 to 60.6%. The initial N<sub>2</sub>O conversion would be in the following order:



This shows that the nature of the composite oxide plays an important role in the Ni-Co catalysts. The increase of catalytic activity with Mg-modified catalyst could be correlated with the decreasing size of Ni-Co particles. This catalyst also shows the highest resistance to fluorine poisoning during the catalytic runs. As revealed by Fig. 2, the presence of Mg in the catalyst avoids deactivation, maintaining the conversion at the initial level during the time-on-stream. In contrast, for Ni-Co-Ti, a significant deactivation was measured, exhibited by a conversion drop from 38.3 to 23.8% during the 12 hours.

### Catalyst deactivation

In this study, poisoning are the most probable reasons accounting for catalyst deactivation. To describe the phenomena of catalyst deactivation more precisely, the authors try to correlate catalytic activity with duration on stream. It has been reported that the decomposition of N<sub>2</sub>O reaction is first order (Pirngruber et al., 2006). The deactivation rate,  $r_d$ , can thus be expressed as a function of activity, as follows:

$$-da/dt = k_d a \quad (1)$$

Eq. (1) can be integrated to yield

$$\ln \frac{a_o}{a} = k_d t$$

Where,  $a_o$  is defined as initial TOF (turnover frequency),  $a$  is TOF at  $t$  (time on stream) and  $k_d$  is the deactivation rate constant.

As shown in Fig. 3, the plot of  $\ln \frac{a_o}{a}$  versus  $t$  showing fairly linear fitting coincides with the assumption of the first order deactivation model. The slope of each line thus obtained from the plot, equivalent to the deactivation rate constant, can be regarded as a criterion to discriminate the efficiency in retarding catalyst deactivation.

The values of  $k_d$  for various catalysts are listed in Table

1. It can be deduced that the MgO-modified catalyst not only gives a high initial activity, but also a low deactivation rate. In contrast, the Ti-modified catalyst is the poorest in stabilities. The deactivation rate constant of various catalysts is in the order: Ni-Co-Mg < Ni-Co-Ca < Ni-Co-Ba < Ni-Co-Mn < Ni-Co-Fe < Ni-Co < Ni-Co-Ti.

#### catalysts.4 Conclusion

Decomposition of  $N_2O$  reaction was studied over Ni-Co-M (M= Mg, Ca, Ba, Ti, Fe, Mn) metal oxides catalysts. The Ni-Co-Mg catalyst has been suggested to be optimal, as it not only enhances catalytic activity, but also retards catalyst deactivation, which results predominantly from fluorine poisoning. The present study suggests that the Ni-Co-Mg catalyst is an excellent catalyst to remove  $N_2O$  via direct decomposition in high fluorine concentration in CVD process of semiconductor industry.

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Table 1. Deactivation rate constants of various catalysts.

Sample	Ni-Co-Mg	Ni-Co-Ca	Ni-Co-Ba	Ni-Co-Mn
$K_d$ (1/h)	0.00106	0.00547	0.00635	0.00734
Sample	Ni-Co-Fe	Ni-Co	Ni-Co-Ti	
$K_d$ (1/h)	0.01007	0.01211	0.0342	

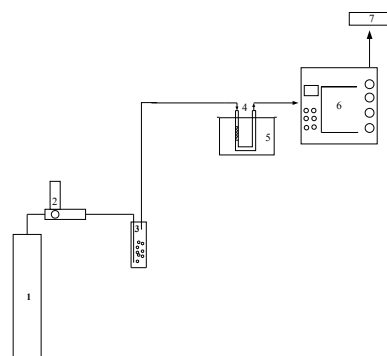


Fig 1. Schematic diagram of test apparatus. (1) 5%  $N_2O$  gas; (2) mass flow control; (3) HF solution; (4) catalyst packing column; (5) heating oven; (6) GC-TCD; (7) Hood.

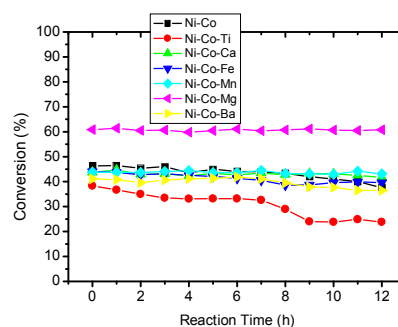


Fig. 2. Deactivities of various catalysts. ( Reaction temperature  $400^{\circ}C$ , WHSV  $45 \text{ mL/mg} \cdot \text{h}$ , 5%  $N_2O$ , 600pmm HF, 2.5%  $H_2O$ )

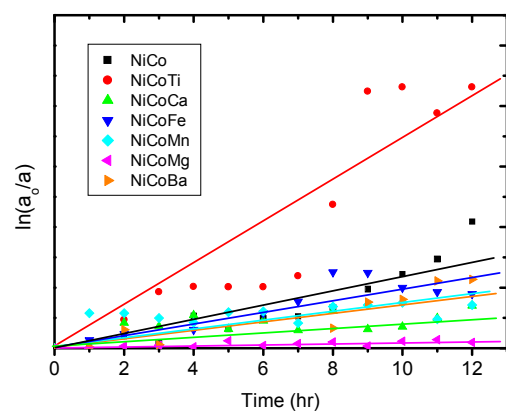


Fig. 3. Test for the first-order deactivation.