

## The effect of Si poisons on $\text{Co}_3\text{O}_4\text{-CeO}_2$ catalyst: comparison with a $\text{Pt/Al}_2\text{O}_3$ catalyst

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### Abstract

The effect of Si poison on conventional  $\text{Pt/Al}_2\text{O}_3$  catalyst and newly developed  $\text{Co}_3\text{O}_4\text{-CeO}_2$  catalyst have been investigated. The effect of Si poison deactivation on the  $\text{Co}_3\text{O}_4\text{-CeO}_2$  catalyst was smaller than that on the  $\text{Pt/Al}_2\text{O}_3$  catalyst. Hexamethyldisilazane (HMDS) was used as a model compound to simulate gaseous silicon poisoning. It was suggested that the small amount of Si species (except  $\text{SiO}_2$ ) negatively influenced the Pt catalyst activity. Most of the HMDS was converted into  $\text{SiO}_2$  during the reaction, which covered the surface of both catalysts. The  $\text{SiO}_2$  was removed when the catalysts were subjected to air blowing treatment.

**Keywords:** odor control, Si poison,  $\text{Co}_3\text{O}_4\text{-CeO}_2$ , honeycomb catalyst, noble metal free, VOCs

### 1. Introduction

Volatile Organic Compounds (VOCs) cause environmental, health and odor problems (Browning, 1965; Lund, 1971), and therefore their degradation has garnered much attention. A major source of man-made VOCs is solvents, e.g., those used in processes such as spray painting, laundry, and offset printing.

Catalytic degradation of VOCs is a very efficient method because of the lower temperature (250-350°C) for oxidation of VOCs in comparison to the temperature (750-850°C) for thermal oxidation (non-catalytic). Pt, which is generally deposited on alumina, is most widely used as a catalyst because of its high catalytic performance (Kummer, 1980; Papaefthimiou, Ioannides & Verykios, 1998; Tang, Lin, & Tan, 1999; Grbic, Radic, & Terlecki-Baricevic, 2004; Tsou, Magnoux, Guisnet, órfão, & Figueiredo, 2005; Bueno-López, Krishna, & Makkee, 2008; Musialik-Piotrowska & Landmesser, 2008). We previously reported that  $\text{Co}_3\text{O}_4\text{-CeO}_2$  catalysts could be used as a substitute for Pt-based catalysts (Somekawa, Yuliati, Ishikawa, Takanabe, & Domen, 2010). The  $\text{Co}_3\text{O}_4\text{-CeO}_2$  catalyst is cheaper than the Pt-based catalyst, and its performance for VOC oxidation is almost the same as that of the Pt-based catalyst.

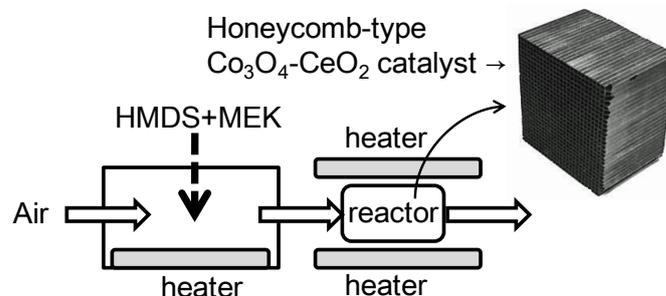
Some industrial outgases contain catalyst poisons such as Si species, which cause deactivation of the catalysts. To prevent the

deactivation of the catalysts, pre-treatment materials (e.g., alumina balls) are sometimes placed in the front of the catalyst chamber. However, these may cause pressure loss and increase the size of the system. Moreover, a small amount of the poison still bypasses the pre-treatment materials, resulting in deactivation of the catalysts. Some researchers have reported the deactivation effect of Si poisoning on Pt-based catalytic activity using HMDS (Windawi & Zhang, 1996; Libanati, Ullenius, & Pereira, 1998; Arnby et al., 2004; Larsson et al., 2007). In these reports, it was stated that the catalytic deactivation was mainly caused by the Si species that covered the Pt active sites.

In this study, the effects of Si poison on  $\text{Co}_3\text{O}_4\text{-CeO}_2$  and  $\text{Pt/Al}_2\text{O}_3$  catalysts were investigated using HMDS. There are currently no other references reporting the effect of Si poisons on the surface of  $\text{Co}_3\text{O}_4\text{-CeO}_2$  catalysts.

### 2. Experimental

Two samples were used: the  $\text{Co}_3\text{O}_4\text{-CeO}_2$  catalyst [Co/Ce (mol ratio = 1)] and a commercial  $\text{Pt/Al}_2\text{O}_3$  catalyst (Pt: 2g/L), which were deposited on honeycomb-type ceramics [length: 25 mm; width: 38 mm; cell size: 1 mm (400 cells per  $\text{inch}^2$ )]. The  $\text{Co}_3\text{O}_4\text{-CeO}_2$  honeycomb-type catalyst is shown in Figure 1.



**Figure 1** Schematic figure of the Si poisoning investigation system (the Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> honeycomb-type catalyst is shown in the upper right)

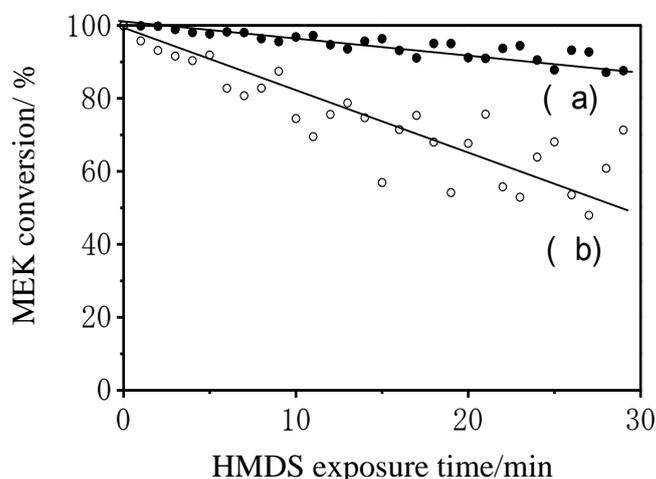
The Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> honeycomb-type catalyst was prepared by the wet-impregnation method using an aqueous solution containing Co and Ce species as precursors. The honeycomb-type ceramics body was dipped into the solution for 1 min. After removal from the solution, it was dried at 100°C for 1 h, and then calcined at 550°C for 1 h. The honeycomb-type ceramics body and the Pt/Al<sub>2</sub>O<sub>3</sub> honeycomb-type catalyst were purchased from Niki-universal c.p. The latter is used at industrial factories generally to clean out gases.

The deactivation process was designed using hexamethyldisilazane (HMDS) as a model compound to simulate gaseous silicon poisoning. Methyl ethyl ketone (MEK) was used as a reactant in order to investigate the catalyst oxidation ability, and also as a solvent for HMDS. The mixture of HMDS and MEK was introduced by a syringe pump (10 µL/min) onto a plate-type heater set inside a stainless box, which was connected to the front of the reactor as shown in Figure 1. Dried air (5 L/min) was introduced into the reaction system. The catalyst was heated at 350°C using a mantle-type heater placed around the reactor. The MEK concentrations at the front and back of the reactor were monitored using proton ionization detectors (RAE Systems). X-ray photoelectron

spectroscopy (XPS) measurements were performed with a PHI Quantera II ESCA spectrometer with monochromatized Al K $\alpha$  radiation. The etching of the samples was carried out using Ar ion (4 kV, 2 mm  $\times$  2 mm). Atomic mapping images were obtained by a PL2300 and EDX6600 scanning electron microscopy energy diffraction X-ray system (SEM-EDX).

### 3. Results and discussion

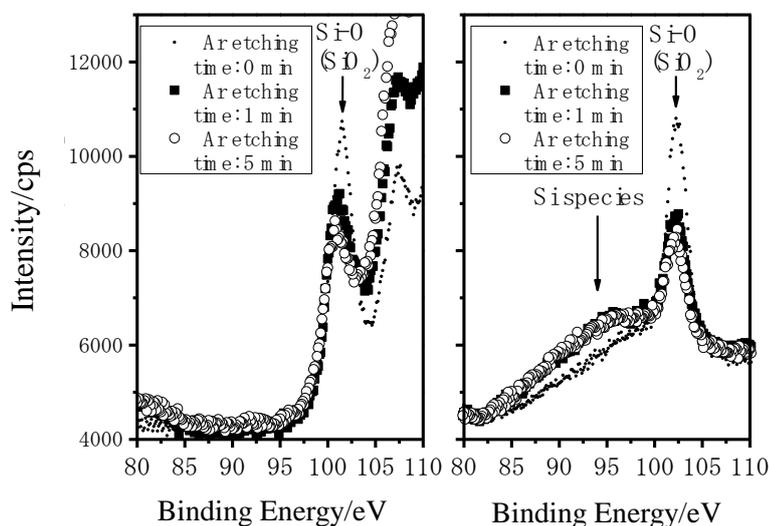
The conversion of MEK at 350°C over the Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> (a) and Pt/Al<sub>2</sub>O<sub>3</sub> (b) honeycomb-type catalysts in the presence of HMDS is shown in Figure 2. The deactivation process is clearly observed as a decreasing MEK conversion with increasing HMDS exposure time for both catalysts. The conversion of the Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts started at complete conversion. The conversion of the Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> catalyst decreased from 100% to ca. 89% after a 30 min exposure. The deactivation of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was more significant than that of the Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> catalyst, the conversion falling from 100% to ca. 55% during the same time period. Thus, it is confirmed that the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is more susceptible to Si poisoning than the Co<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> catalyst.



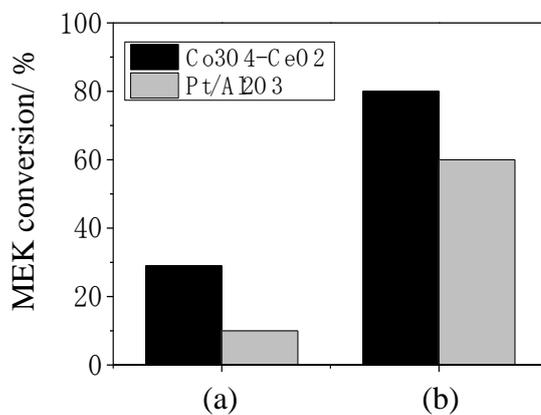
**Figure 2** MEK conversion vs HMDS exposure time; [MEK: ca.200 ppm; HMDS: ca. 10 ppm; flow gas: air, 5L/min; reaction temperature: 350°C; catalyst:  $\text{Co}_3\text{O}_4\text{-CeO}_2$  (a) and  $\text{Pt/Al}_2\text{O}_3$ (b) honeycomb-type catalysts (31 mL)]

The surface composition of these deactivated samples was studied by XPS analysis as shown in Figure 3. The intensity of the C 1s peak (at 284-285 eV) is used as a reference. The XPS spectra of both deactivated samples have Si 2p peaks around 103 eV, indicating that  $\text{SiO}_2$  exists on the catalyst surface. It is suggested that both samples are covered by  $\text{SiO}_2$ , which causes the deactivation of the catalyst by blocking the active sites. There is a shoulder at around 94 eV only in the deactivated  $\text{Pt/Al}_2\text{O}_3$  sample, which is attributed to Si species other than  $\text{SiO}_2$  (A. Larsson et al., 2007). Therefore, it is suggested that the Si species accelerated the catalytic deactivation. The peak (Si species) increased after Ar ion sputtering (1 min and 5 min) as shown in Figure 3. Only  $\text{SiO}_2$  peaks were observed on the  $\text{Co}_3\text{O}_4\text{-CeO}_2$  catalyst. One of the reasons for small effect of the Si deactivation on  $\text{Co}_3\text{O}_4\text{-CeO}_2$  catalyst may be the weak chemical bonding interaction of the Si-(metal oxides) bonds comparison with that of the Si-Pt bonds. The larger surface area of the  $\text{Co}_3\text{O}_4\text{-CeO}_2$  may also contribute to suppression of Si deactivation.

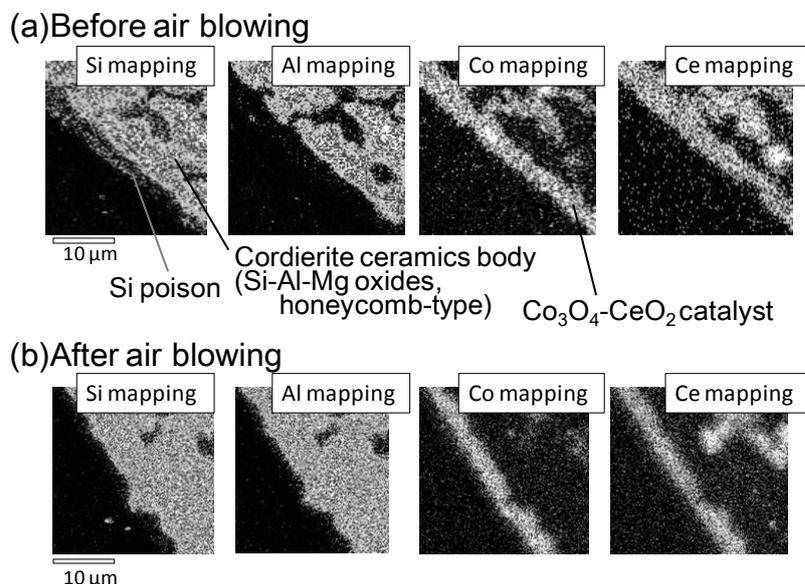
After 5 h of treatment with Si, the conversions of the  $\text{Co}_3\text{O}_4\text{-CeO}_2$  and the  $\text{Pt/Al}_2\text{O}_3$  catalysts were down to 29% and 10%, respectively. However the conversion of these catalysts recovered to 80% and 61%, respectively, after simply blowing air over the catalysts (5 L/min) at room temperature for 24 h as shown in Figure 4. This suggests that these catalysts were only weakly covered by  $\text{SiO}_2$ , and therefore the  $\text{SiO}_2$  was exfoliated by the air blowing treatment. Cross-sectional images of the  $\text{Co}_3\text{O}_4\text{-CeO}_2$  catalysts are shown in Figure 5. The thickness of the  $\text{Co}_3\text{O}_4\text{-CeO}_2$  layer is ca. 5  $\mu\text{m}$ . The  $\text{Co}_3\text{O}_4\text{-CeO}_2$  is coated on the honeycomb-type ceramics body (cordierite: Si-Al-Mg oxides). In deactivated samples before the air blowing treatment, Si was distributed over the entire  $\text{Co}_3\text{O}_4\text{-CeO}_2$  side (it overlaps with the catalyst because the catalyst is porous). After air blowing treatment, Si could not be found on the catalyst side, suggesting that  $\text{SiO}_2$  was exfoliated by the air blowing treatment.



**Figure 3** XPS spectra of the  $\text{Co}_3\text{O}_4\text{-CeO}_2$  catalyst (a) and the  $\text{Pt/Al}_2\text{O}_3$  (b) catalysts. Ar ion sputtering: 0, 1, 5 min



**Figure 4** MEK conversion before (a) and after (b) air blowing treatment (24 h). The catalysts were exposed to the Si poison for 5 h



**Figure 5** SEM-EDX cross-sectional images (Si and Co mapping) of the catalysts exposed before (a) and after (b) the air blowing treatment

#### 4. Conclusion

In this report, we determined that  $\text{Co}_3\text{O}_4\text{-CeO}_2$  is more resistant to Si poisoning than  $\text{Pt/Al}_2\text{O}_3$ . This is an important discovery, since some factory outgases contain Si compounds. We expect that these findings will enable the spread of low-cost Si poison-resistant catalysts for air pollution control in the near future.

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