

## A - 2.2.4 Development of Techniques for Decomposition of Brominated Organic Compounds

**Contact Person** Takashi Ibusuki  
Director  
Atmospheric Environmental Protection Department  
National Institute for Resources and Environment  
16-3 Onogawa, Tsukuba, Ibaraki, 305-8569 Japan  
Tel:+81-298-58-8250 Fax:+81-298-58-8258  
e-mail:ibusuki@nire.go.jp

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**Abstract** Three different methods were investigated for the abatement of bromomethane emitted from stationary sources such as quarantine facilities: catalytic decomposition, nonthermal plasma chemical decomposition, and photocatalytic decomposition. In the catalytic decomposition of bromomethane, Cu-doped  $\text{WO}_3/\text{Al}_2\text{O}_3\text{-ZrO}_2$  was the most effective catalyst to promote its oxidative decomposition at  $400^\circ\text{C}$ . Nonthermal plasma afforded a reaction medium where 1,000 to 2,000 ppm of bromomethane in  $\text{N}_2\text{-O}_2$  (98:2 v/v) was decomposed in higher than 90 % conversions at 1.5 to 4.4 s of residence time. Practical application of this method is promising because 1,000 ppm of bromomethane in dry  $\text{N}_2$  can be decomposed almost quantitatively at 0.9 s of residence time with a pulsed corona reactor on a semibench scale. The initial concentration of bromomethane affected its photocatalytic decomposition behavior, and 2,000 ppm of bromomethane was completely photodecomposed in 8 h with a newly prepared  $\text{TiO}_2$  catalyst, HDep.

**Key Words** Bromomethane, Decomposition, Catalyst, Nonthermal plasma, Photocatalyst

### 1. Introduction

Bromomethane, which is one of the most superior fumigants, has been produced and consumed even after the production of chlorofluorocarbons was completely prohibited in 1996 for the prevention of stratospheric ozone depletion. Development of bromomethane-decomposition technologies is urgently required for its safe treatment on agricultural fields and in quarantine facilities.

### 2. Research Objective

This study aimed at developing efficient methods for the decomposition of bromomethane in effluent gases at the sites of its utilization. Three different methods were selected for this study, i.e. catalytic decomposition, nonthermal plasma chemical decomposition, and photocatalytic decomposition.

### 3. Research Methods

#### 3.1. Catalytic decomposition

$\text{WO}_3/\text{Al}_2\text{O}_3\text{-ZrO}_2$  catalyst was prepared as in the previous paper<sup>1)</sup>. The oxidative

decomposition of bromomethane was carried out with a fixed-bed reactor using feed gas of the bromomethane (1 %), oxygen (17 %), and nitrogen (82 %) mixture. The flow rate was 90 cm<sup>3</sup>/min. The weight of catalyst charged in the reactor was 1.0 g. The reaction temperatures ranged from 400 to 600°C. The products were analyzed by GC.

### 3.2. Nonthermal plasma chemical decomposition

Two types of plasma reactors were used: a laboratory-scale ferroelectric packed-bed reactor with BaTiO<sub>3</sub> pellets (1 mm in diameter,  $\epsilon=5,000$ ) and a semibench-scale pulsed corona reactor. Reactant gases containing bromomethane were introduced to the reactors with sets of mass flow controllers and gas mixers. A small volume of bubbler was used for reactant gas humidification. The byproducts were identified by GC-MS. Bromomethane conversions and the byproduct yields were determined by GC and a chemiluminescent NO<sub>x</sub> analyzer.

### 3.3. Photocatalytic decomposition

Commercial photocatalysts (P25 and ST-01) and our developed photocatalyst (we called HDep) were used for the decomposition of bromomethane. P25 and ST-01 were white powder; 1.6 g of photocatalyst powder was used for photoreaction. On the other hand, HDep was prepared from titanium alkoxide. TiO<sub>2</sub> was formed with heat decomposition of titanium alkoxide onto glass substrate as film. TiO<sub>2</sub> weight on glass substrate was around 60 mg. The size of glass substrate was 10 x 10 cm. Irradiation light source was 10 W of blacklight bulb, and light intensity was around 0.2 mW/cm<sup>2</sup> ( $\lambda = 365$  nm). The initial concentration of bromomethane was 2,000 or 5,000 ppm.

## 4. Results and Discussion

### 4.1. Catalytic decomposition

Bromomethane was decomposed completely at temperatures above 500°C, but it was not decomposed at 400°C. A large portion of carbon oxides, the decomposition products, were CO at temperatures investigated. The ratio of CO<sub>2</sub> to CO increased with an increase in temperature. These findings suggest that bromomethane is difficult to be oxidized into CO<sub>2</sub>.

The oxygen concentration in the feed gas was increased from 17 to 33 % at 400°C to promote the decomposition of bromomethane. It was found that the conversion of bromomethane was improved to a high value over 90 % and the catalytic deactivation did not occur. But the ratio of CO<sub>2</sub> to CO did not increase.

The WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst was modified by doping with another metal to increase the ratio of CO<sub>2</sub> to CO. The metals investigated were Co, Ni, Mn, Pt, and Cu. The amount of a doped metal was 0.5 wt%. It was found that a remarkable increase in the selectivity to CO<sub>2</sub> was obtained with the catalysts doped with Pt or Cu (Fig. 1-A) and an increase in the conversion of bromomethane was obtained with the catalysts doped with Co or Cu. (Fig. 1-B). After all, it has been concluded that the WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst doped with Cu is the most effective for the oxidative decomposition of bromomethane.

### 4.2. Nonthermal plasma chemical decomposition

1,000 ppm to 1 % of bromomethane could be decomposed in nonthermal plasma with a packed-bed reactor. Bromomethane conversion decreased with its initial concentration, but its decrements were relatively small. Bromomethane was more reactive in dry N<sub>2</sub> than in dry air. This kind of rate-depressing effect was observed also in the plasma chemical

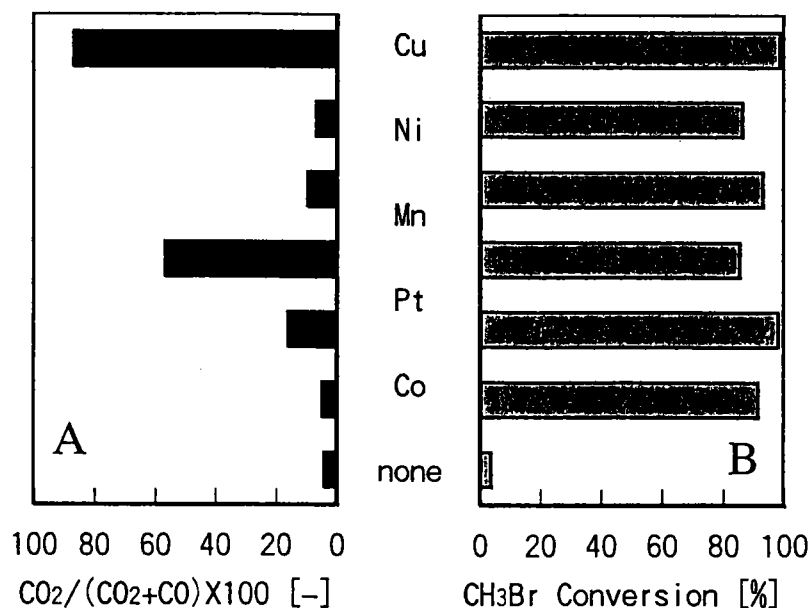


Fig. 1 Effect of metal doping over WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst on CH<sub>3</sub>Br decomposition  
Flow rate 90 cm<sup>3</sup>/min; feed gas CH<sub>3</sub>Br:N<sub>2</sub>:O<sub>2</sub> = 1:59:30; reaction temperature 400°C

decomposition of trichloroethylene, tetrachloroethylene, etc. Figure 2 shows that bromomethane conversion decreases with oxygen content in the background gas composed of N<sub>2</sub> and O<sub>2</sub>. Gas humidification lowered bromomethane conversions at similar input energy densities (J/L) (= primary power (W)/gas flow rate (L/s)). The negative effect of O<sub>2</sub> and water in nonthermal plasma media suggests that the predominant process for the initial decomposition of bromomethane could be non-oxidative bond cleavage in the excited state of bromomethane formed directly and/or indirectly through energy transfer from high-energy electrons via the excited state of N<sub>2</sub>.

Similar byproduct distributions were obtained, irrespective of plasma reactors used. Major byproducts obtained in dry N<sub>2</sub> were methane, methanol, cyanogen bromide, dibromomethane, and tribromomethane. N<sub>2</sub> humidification decreased the yields of the brominated byproducts, while those of methane and methanol increased. On the other hand,

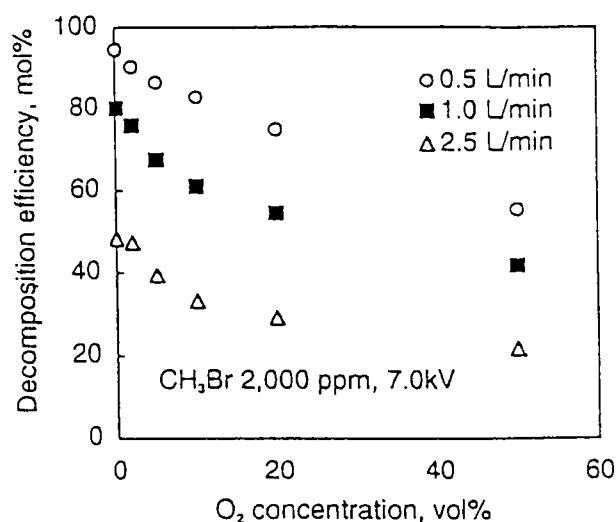


Fig. 2 Effect of Oxygen content in the N<sub>2</sub>-O<sub>2</sub> background gas on CH<sub>3</sub>Br conversion

only small amounts of the above byproducts were detected in air, irrespective of humidification. These findings suggest that oxygen sources such as  $O_2$  and water in nonthermal plasma play important roles both in the suppression of nitrogen incorporation into byproducts and in the oxygenation of reaction intermediates such as carbon radicals formed in the initial homolytic decomposition of bromomethane.

Nitrogen oxides can be also formed as byproducts in nonthermal plasma chemical processing of hazardous air pollutants. Figure 3 shows the effect of oxygen content in  $N_2$ - $O_2$  on  $NO_x$  formation. Oxygen content is a key factor controlling  $NO_x$  levels, and formation of  $NO_x$  accompanied by the decomposition of bromomethane could be suppressed in the presence of 2 % of  $O_2$ . As observed in Fig. 2, replacement of 2 %  $N_2$  by  $O_2$  caused only small decrements in bromomethane conversion. Practical operating conditions could be achieved by controlling effluent gas composition.

With packed-bed and pulsed corona reactors, almost no differences were observed in the effects of  $O_2$  and water on bromomethane conversion and byproduct distribution. Thus, nonthermal plasma chemical decomposition of bromomethane in  $N_2$  was carried out with a pulsed corona reactor on a semibench scale. Figure 4 shows that 1,000 ppm of bromomethane can be decomposed effectively at 40 L/min of gas flow rate.

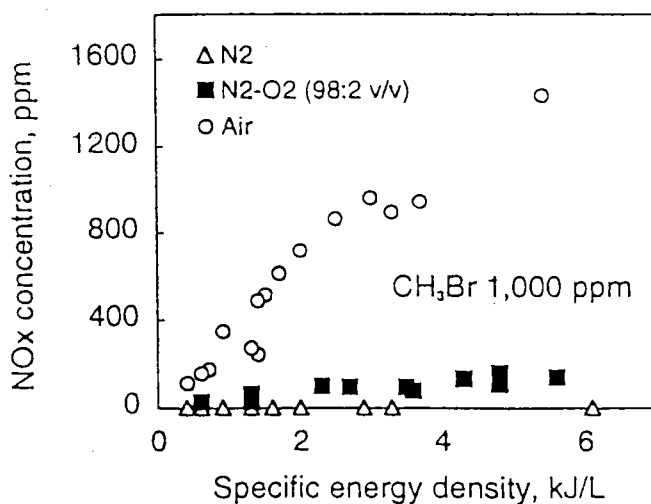


Fig. 3 Effect of oxygen content in  $N_2$ - $O_2$  background gas on  $NO_x$  formation

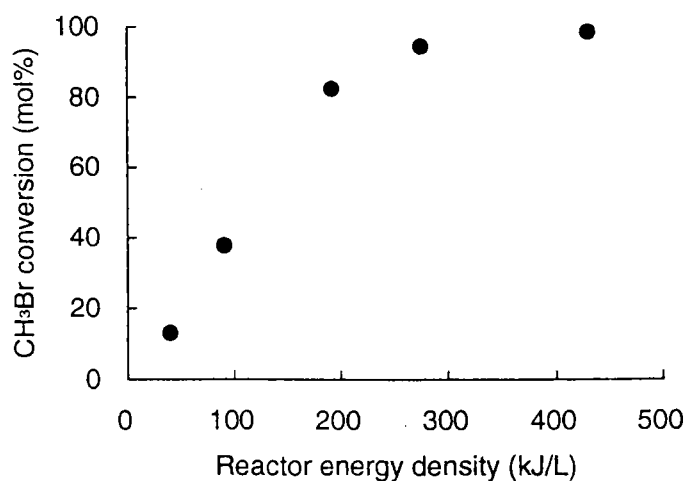


Fig. 4  $CH_3Br$  decomposition in  $N_2$  with a pulsed corona reactor

### 4.3. Photocatalytic decomposition

Approximately, a few minutes after the injection of saturated gas into the reaction system, adsorption equilibrium was reached, and irradiation was started. HDep and ST-01 easily decomposed around 2,000 ppm bromomethane (Fig. 5). 2,000 ppm bromomethane was completely removed at around 4 to 8 h. On the other hand, P25 was needed over 8 h to remove bromomethane. Under low concentration system, the reaction obeyed mass transfer-controlled first order kinetics. When the initial concentration was set at around 2,000 ppm and blacklight was used, an exponential concentration decrease was observed just after the irradiation. Bromomethane was scarcely decomposed by light without photocatalyst.

Decreasing ratio of around 5,000 ppm bromomethane was slower than low concentration of bromomethane by using photocatalyst. However, formation of  $\text{CO}_2$  derived from decomposition of bromomethane was observed on the photocatalyst used system. In the case of high concentration system, the concentration change did not show an exponential decay. This was probably because the initial concentration was too high as compared to the incident photon number so that the reaction initially proceeded with zero-order kinetics, i. e., light intensity-controlled kinetics. In this system, light source power was relatively weak. If we use more strong light source such as sunlight (approximately 0.1 to 4  $\text{mW}/\text{cm}^2$ ), photodecomposition ratio of bromomethane must be accelerated.

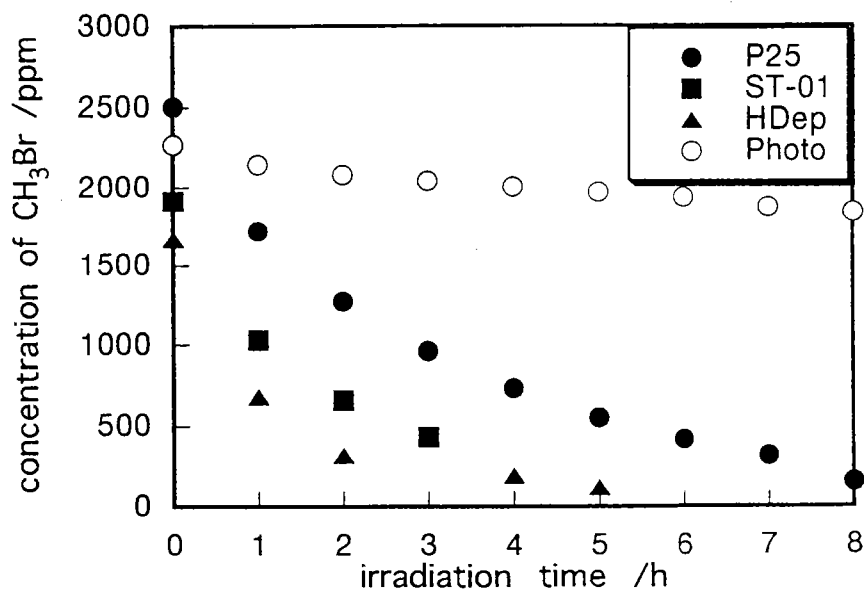


Fig. 5  $\text{TiO}_2$ -catalyzed photodecomposition of  $\text{CH}_3\text{Br}$

### Reference

- 1) H. Nagata et al., *J. Jpn. Petrol. Inst.*, **37**, 209 (1994).