



## Improvement in heat resistance of NO<sub>x</sub> trap catalyst using Ti–Na binary metal oxide as NO<sub>x</sub> trap material

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### ARTICLE INFO

#### Article history:

Received 1 October 2009

Received in revised form 7 January 2010

Accepted 13 January 2010

Available online 20 January 2010

#### Keywords:

NO<sub>x</sub> trap catalyst

Alkali metals

Alkaline earth metals

Na

Ti

Binary metal oxide

Heat resistance

### ABSTRACT

The purpose of this study was to identify suitable base materials for NO<sub>x</sub> trap catalysts from the viewpoint of heat resistance. First, suitable elements among alkali metals (M: K, Na, Li) and alkaline earth metals (M: Ba, Ca, Sr, Mg) were evaluated using M–Rh,Pt/Al<sub>2</sub>O<sub>3</sub>. Na was found to be the most suitable element that combines NO<sub>x</sub> trap performance with hydrocarbon purification performance after heat treatment at 973 K. Moreover, the effects of binary metal oxides with Na and M' (Zr, Fe, W, Mo, Ti) were evaluated to improve the heat resistance of Na–Rh,Pt/Al<sub>2</sub>O<sub>3</sub>. The ranking of the NO<sub>x</sub> trap activity of M' was Ti > none > Fe > W > Zr > Mo; Ti was the most suitable additional element for improving heat resistance of Na–Rh,Pt/Al<sub>2</sub>O<sub>3</sub>. The maximum amount of NO<sub>x</sub> conversion and the maximum number of base sites of Ti,Na–Rh,Pt/Al<sub>2</sub>O<sub>3</sub> were reached at a Ti/Na mol ratio of 0.1. It was inferred that the addition of Ti to Na–Rh,Pt/Al<sub>2</sub>O<sub>3</sub> formed a Ti–Na binary metal oxide from catalyst characterisation by X-ray diffraction and X-ray photoelectron spectrometry, and this Ti–Na binary metal oxide improved the thermal stability of Na–Rh,Pt/Al<sub>2</sub>O<sub>3</sub>. Finally, from vehicle tests, it was clear that the NO<sub>x</sub> trap catalyst, which supported Ti–Na binary metal oxide, exhibited high heat resistance.

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## 1. Introduction

Two results from the reduction of CO<sub>2</sub> emissions, i.e., decrease in fuel consumption, and improvement in exhaust gas purification for automobiles, are desirable for environmental protection. The lean (air-fuel ratio > 18) combustion method used for gasoline engines and the propulsion method used for diesel engines are effective in decreasing fuel consumption. However, nitrogen oxides (NO<sub>x</sub>) in the exhaust gas cannot be efficiently removed using a conventional three-way catalyst because a large amount of oxygen is present in the exhaust gas.

Therefore, NO<sub>x</sub> trap catalysts were studied as an alternative and effective NO<sub>x</sub> purification method [1–4]. NO<sub>x</sub> trap catalysts generally contain precious metals and base materials on support materials such as alumina [5,6]. This type of catalysts requires lean-rich engine management. In a lean condition, NO is mainly oxidised to NO<sub>x</sub> on precious metals, and the generated NO<sub>x</sub> is mainly trapped by the base materials. Next, by switching to a rich condition (air-fuel ratio < 14.7), the trapped NO<sub>x</sub> is reduced on the

precious metals by CO and hydrocarbons (HC) in the exhaust gas. Therefore, there has been considerable interest in these catalysts for lean burn gasoline and diesel engines [7].

Matsumoto et al. [8] studied NO<sub>x</sub> trap catalysts that supported alkali metals or alkaline earth metals on Pt/Al<sub>2</sub>O<sub>3</sub>, and concluded that Ba was the most suitable NO<sub>x</sub> trap material from the viewpoint of simultaneously obtaining good NO<sub>x</sub> trap ability and HC purification performance. Furthermore, they pointed out that SO<sub>x</sub> in the exhaust gas converted the NO<sub>x</sub> trap elements to sulphates, and the sulphates could no longer trap NO<sub>x</sub>. Since their work, there have been a number of studies on the NO<sub>x</sub> trap mechanism [9–11] and SO<sub>x</sub> durability of Pt/Ba/Al<sub>2</sub>O<sub>3</sub> [12,13].

When a vehicle is driven with a high load, the temperature of the exhaust gas rises to 973 K. Therefore, the NO<sub>x</sub> trap catalyst with good NO<sub>x</sub> purification performance at 673 K and heat resistance at 973 K is necessary. It was reported that NO<sub>x</sub> trap catalyst with K, whose base strength is stronger than that of Ba, improved the fresh NO<sub>x</sub> trap ability above 673 K because the NO<sub>x</sub> trap ability of Ba decreases above 623 K [14]. However, the high temperature causes thermal deterioration of the NO<sub>x</sub> trap catalyst because of the sintering of precious metals and the reaction of alumina with K and Ba as NO<sub>x</sub> trap elements [15–17]. There have been some studies on a method to improve the thermal stability of

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K from the viewpoint of inhibiting the reaction of alumina with K [18–20]. Hachisuka et al. [18] pointed out that ZrO<sub>2</sub>–TiO<sub>2</sub> support, which maintained a high specific surface area after heat treatment at 1073 K, improved the thermal stability of K and precious metals. Moreover, MgAl<sub>2</sub>O<sub>4</sub> [19] and Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>–TiO<sub>2</sub> [20] were reported to support the thermal stability of K.

The purpose of this study was to improve NO<sub>x</sub> trap material from the viewpoints of NO<sub>x</sub> trap performance at 673 K and heat resistance.

First, the most suitable element with respect to heat resistance at 973 K among alkaline metals and alkaline earth metals was evaluated with M–Rh,Pt/Al<sub>2</sub>O<sub>3</sub> (M: K, Na, Li, Ba, Ca, Sr, Mg) because the heat treatment temperature was indefinite in a previous study [8].

Next, to improve the heat resistance of M–Rh,Pt/Al<sub>2</sub>O<sub>3</sub>, the effects of binary metal oxides with M' (M' = Zr, Fe, W, Mo, Ti) were investigated. Third, the basicity, the number of base sites, the electronic states, and X-ray crystal structure were examined for characterisation of the binary metal oxide with CO<sub>2</sub> temperature programmed desorption (CO<sub>2</sub> TPD) using an X-ray photoelectron spectrometer (XPS). Finally, the heat resistance catalyst was verified in vehicle tests.

## 2. Experimental

### 2.1. Catalyst preparation

The catalytic elements were precious metals (Rh, Pt), alkali metals (K, Na, Li), alkaline earth metals (Ba, Ca, Sr, Mg), and transition metals (Zr, Fe, Ti, W, Mo). These catalytic elements were supported on alumina-coated cordierite honeycombs (Nihongaiishi, 400 cells/in<sup>2</sup>) using an impregnation method. Pt and Rh were provided by Tanaka Kikinzoku as [Pt(NH<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> solution and Rh nitrate solution. Materials provided by Wako Pure Chemicals were LiNO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Sr(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, (CH<sub>3</sub>COO)<sub>2</sub>Ba, ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O. Titania sol was provided by Sakai Chemical Industry, and ammonium metatungstate solution was provided by Nippon Inorganic Colour & Chemical. As an example, Na–Rh,Pt/Al<sub>2</sub>O<sub>3</sub> was prepared using the following steps. (1) A wash-coat was deposited by immersing the cordierite honeycomb into an aqueous slurry of boehmite (Sasol, Pural SB). (2) Pt and Rh were supported on the alumina-coated cordierite honeycomb using an impregnation method. The amount of Pt in the alumina-coated honeycomb was 2.8 g/L, and that of Rh was 0.1 g/L. (3) Na was supported on Rh,Pt/Al<sub>2</sub>O<sub>3</sub> using the same impregnation method. In each step, the catalyst was dried with a hot air flow, calcined at 873 K for 1 h in an electric furnace, and finally calcined at 973 K for 5 h.

### 2.2. Catalyst evaluation using model exhaust gas

An ordinary fixed-bed flow reactor was used to examine the catalytic activity of the prepared catalysts. A catalyst (6 cm<sup>3</sup>) was placed in a quartz tubular reactor (inner diameter: 28 mm) with a thermocouple placed 10 mm upstream from the catalyst. The catalyst inlet temperature was controlled with an electric furnace, which was vertically fixed to the outside of the tubular reactor. The catalytic performance was measured by exposing the catalyst to synthetic gas mixtures for lean and rich operations, which were controlled with mass flow controllers. Table 1 lists the composition of the lean and rich synthetic gas mixtures. The lean and rich gas flow rate was 3000 cm<sup>3</sup>/min (SV: 30,000 h<sup>−1</sup>).

A steady state experiment was carried out to determine the NO<sub>x</sub> trap amount of the catalyst under lean operation. The inlet gas temperature was 673 K.

**Table 1**

Composition of lean and rich simulated experimental gas mixtures.

Gas type	Lean	Rich
NO (ppm)	600	1,000
C <sub>3</sub> H <sub>6</sub> (ppm)	500	600
CO (ppm)	1,000	6,000
CO <sub>2</sub> (ppm)	10	12
O <sub>2</sub> (%)	5	0.5
H <sub>2</sub> (ppm)	0	3,300
H <sub>2</sub> O (%)	10	10
N <sub>2</sub>	Balance	Balance
SV (h <sup>−1</sup> )	30,000	30,000

A lean-rich cycling experiment was carried out to determine NO<sub>x</sub> and HC conversions. The inlet gas temperature was 673 K, and lean and rich synthetic gas mixtures were alternately introduced for periods of 3 min. The NO<sub>x</sub> and HC concentrations of the lean or rich atmosphere at the catalyst outlet were measured for 3 min by a chemiluminescence method using an NO<sub>x</sub> analyser; (Horiba CLA-510) and an FID method using an HC analyser (Horiba FIA-510) after beginning the lean or rich synthetic gas flow. NO<sub>x</sub> and HC conversions of lean atmosphere were calculated using Eq. (1).

$$\text{NO}_x \text{ (or HC) conversion (\%)} = \left(1 - \frac{A}{B}\right) \times 100 \dots \quad (1)$$

A: total NO<sub>x</sub> (or HC) concentration of lean atmosphere at the catalyst outlet for 3 min; B: total NO<sub>x</sub> (or HC) concentration of lean atmosphere at the catalyst inlet for 3 min.

### 2.3. Catalyst evaluation in vehicle tests

The catalyst was mounted in a commercial lean burn vehicle with a lean burn engine (displacement: 1.8 L). The lean burn vehicle was set on a chassis dynamometer. Catalytic performance was evaluated at steady speeds from 40 to 80 km/h and using a 10–15 mode running based on the Japan Domestic Testing Act. The lean condition areas in the 10–15 mode running were the fixed speed driving areas (20, 40, 60 and 70 km/h) and an acceleration area. Other areas in the 10–15 mode running were maintained in a rich condition. NO<sub>x</sub> and HC concentrations were measured using an automobile emission analyser (Horiba MEXA-9400).

### 2.4. Catalyst characterisation

#### 2.4.1. CO<sub>2</sub> TPD

CO<sub>2</sub> is adsorbed on solid surface base sites, and the CO<sub>2</sub> adsorption strength is proportional to the basicity [21]. Therefore, the amount of adsorbed CO<sub>2</sub> corresponds to the number of base sites of the catalyst, and the adsorbed CO<sub>2</sub> sequentially desorbs from weak base sites according to the increase in temperature.

The fixed-bed flow reactor was used for evaluations of both CO<sub>2</sub> adsorption amount and TPD. The powder catalyst (1 mg), from the crushed honeycomb-type catalyst, was placed in the quartz tube reactor (inner diameter: 10 mm) with a thermocouple set 10 mm upstream from the catalyst. The CO<sub>2</sub> concentration was measured using a thermal conductivity detector (TCD) (Hitachi G-103).

The CO<sub>2</sub> adsorption experiment was carried out at 373 K. CO<sub>2</sub> was injected into He carrier every 3 min until CO<sub>2</sub> adsorption was saturated as confirmed by TCD. Then the temperature was increased to 673 K at 10 K/min. During this, only He carrier was used.

### 2.5. XRD

An X-ray diffractometer (XRD) (Rigaku RU-200) was used to analyse the crystal state of the sample. The Cu Kα radiation X-ray

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