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Impedancemetric gas sensor based on Pt and WO_3 co-loaded TiO_2 and ZrO_2 as total NO_x sensing materials

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Abstract

Pt-loaded metal oxides [WO_3/ZrO_2, MO_x/TiO_2 ($MO_x = WO_3$, MoO_3, V_2O_5), WO_3 and TiO_2] equipped with interdigital Au electrodes have been tested as a NO_x (NO and NO_2) gas sensor at 500 °C. The impedance value at 4 Hz was used as a sensing signal. Among the samples tested, Pt-WO_3/TiO_2 showed the highest sensor response magnitude to NO. The sensor was found to respond consistently and rapidly to change in concentration of NO and NO_2 in the oxygen rich and moist gas mixture at 500 °C. The 90% response and 90% recovery times were as short as less than 5–10 s. The impedance at 4 Hz of the present device was found to vary almost linearly with the logarithm of NO_x (NO or NO_2) concentration from 10 to 570 ppm. Pt-WO_3/TiO_2 showed responses to NO and NO_2 of the same algebraic sign and nearly the same magnitude, while Pt/WO_3 and WO_3/TiO_2 showed higher response to NO than NO_2. The impedance at 4 Hz in the presence of NO for Pt-WO_3/TiO_2 was almost equal at any O_2 concentration examined (1–99%), while in the case of Pt/WO_3 and WO_3/TiO_2 the impedance increased with the oxygen concentration. The features of Pt-WO_3/TiO_2 are favorable as a NO_x sensor that can monitor and control the NO_x concentration in automotive exhaust. The effect of WO_3 loading of Pt-WO_3/ZrO_2-based sensor is studied to discuss the role of surface W-OH sites on the NO_x sensing.

Keywords: NO_x gas sensor; Impedance; Tungsten oxide; Solid acid

1. Introduction

Solid-state gas sensors to detect NO and NO_2 (NO_x) have been in demand for monitoring and controlling exhaust from automobiles [1–18]. The sensors are required to monitor NO_x ($NO + NO_2$) concentration quickly over a wide range of oxygen and moisture concentrations at high temperatures of ca. 500 °C and above. The mixed-potential type sensor is one of the promising candidates for a practical use. However, the response to NO_2 is much higher than that to NO, and the response to NO_2 is opposite to that to NO [1–6]. The "NO_x" in combustion exhaust is typically a mixture of NO and NO_2. Therefore, so-called "total NO_x sensor" having equal or similar response characteristics to either NO or NO_2 is a suitable NO_x sensor for automobiles. Although there have been various proposals for NO_x sensors by using various sensing materials, there are only a few examples of the NO_x sensors potentially capable to measure total NO_x ($NO + NO_2$) at high temperature [7–18]. Kato et al. [7] first achieved near total-NO_x sensing by lowering O_2 concentration, [O_2], to ~1000 ppm and operating at 700 °C, thus presumably driving the reaction $NO_2 = NO + 1/2O_2$ far to the right. Dutta and co-workers [8,9] used an upstream catalyst to fix the ratio [NO]:[NO_2] prior to impingement on a "mixed-potential" NO_x sensing element. Kunimoto et al. [10] and Miura and co-workers [11] employed "electrochemical NO_x conversion" to NO_2 in a total NO_x sensor with a mixed-potential sensing element. Miura et al. [15–18] reported that impedance-based devices using a YSZ tube and specific spinel-type oxide electrodes could detect total NO_x content in the a sample gas at high temperature (700 °C). These works all incorporated some form of NO_x conversion or equilibration in the design of a total NO_x sensor. West et al. [12] have demonstrated the total

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NO_x sensing characteristics of a new sensing element based on a $La_{0.85}Sr_{0.15}Cr_{1.01}O_3$-electrode and YSZ. The sensor has responses to NO and NO_2 of the same algebraic sign and nearly the same magnitude, though its sensing signal depends on the O_2 concentration. Therefore, the oxygen concentration in the sample gas existing at the space near the NO_x sensing device should be monitored by an O_2 sensor or it should be controlled to be constant at all times.

Tungstated-zirconia (WO_3/ZrO_2) [19–23] and tungstated-titania (WO_3/TiO_2) [24] are well established catalytic materials; WO_3/ZrO_2 is a promising candidate of the key material for solid acid chemical processes and WO_3/TiO_2 is a commercial support material for the selective reduction of NO_x with NH_3. Their surface properties have been well studied by many research groups, and it is established that they have a high surface area (typically 50–100 $m^2\,g^{-1}$), strong acidity and moderate redox property. Structural analysis of these catalysts has revealed that highly dispersed tungstate species are on the oxide support as sub-nanometer sized polytungstate clusters or two dimensional polytungstate monolayers. The uniform and unique structure of the polytungstate clusters may provide a unique sensing property. Previously, we demonstrated that WO_3/ZrO_2 was effective as a sensing material for a selective NH_3 gas sensor [25]. Mechanistic studies showed that the migration of H^+ or NH_4^+ cations on the oxide surface was responsible for the conductivity of WO_3/ZrO_2 in the absence or presence of NH_3 gas, respectively [26].

In this paper, we describe a simple impedancemetric sensor that responds equally to NO and NO_2 without the need for extra NO_x conversion materials. The effects of operating temperature and co-existing gases (H_2O, O_2) on the sensing properties of a Pt-WO_3/TiO_2-based sensor is shown to demonstrate that it works over a wide range of oxygen and moisture concentrations at high temperature (500 °C). The effect of WO_3 loading of the Pt-WO_3/ZrO_2-based sensor is studied to discuss the factor affecting the sensing properties.

2. Experimental

2.1. Preparation of materials

TiO_2 (mainly anatase type, 50 $m^2\,g^{-1}$, JRC-TIO-4) and H-ZSM-5 zeolite (JRC-Z5-25H, $SiO_2/Al_2O_3 = 25$) were supplied by the Catalysis Society of Japan. The WO_3 powder was prepared as follows. An aqueous solution of ammonium paratungstate was neutralized by a dilute nitric acid solution. The precipitate obtained (H_2WO_4) was thoroughly washed with deionized water, and dried at 100 °C for 24 h and then calcined at 600 °C for 3 h. ZrO_2 was prepared by hydrolysis of zirconium oxynitrate 2-hydrate in distilled water by gradual adding an aqueous NH_4OH solution (1.0 mol dm^{-3}), filtration of precipitate, washing with distilled water for three times, and dryness at 100 °C for 24 h in air. WO_3/ZrO_2 was prepared by an impregnation of the obtained hydrated zirconia with an aqueous solution of ammonium paratungstate at pH 10 with an aqueous NH_4OH solution [26]. The suspension was evaporated in a rotary-evaporator. WO_3/TiO_2, MoO_3/TiO_2 and V_2O_5/TiO_2 were prepared, analogously to the preparation of WO_3/ZrO_2, by an impregnation method using TiO_2 powder, ammonium metatungstate, ammonium heptamolybdate, and ammonium vanadium oxide (oxalic acid added to improve the solubility). The solid thus obtained was dried at 100 °C for 24 h and then calcined at 600 °C for 3 h. Loading of the metal oxides (WO_3, MoO_3 and V_2O_5) was 10 wt.%. Platinum (0.5 wt.%) loading on these oxides and other oxides (TiO_2, WO_3, H-ZSM-5) was performed by an impregnation method using aqueous solutions of $Pt(NH_3)_4Cl_2$, and the sample was finally calcined at 600 °C for 2 h.

2.2. Material characterizations

The amount of acid sites was determined from in situ FT/IR spectra of NH_3-adsorbed samples using a JASCO FT/IR-620 equipped with a quartz IR cell connected to a conventional flow reaction system [26]. The WO_3/ZrO_2 powder was pressed into a 0.05 g wafer and mounted into the quartz IR cell with KBr windows. The sample was heated in O_2(10%)/N_2(balance) at 500 °C for 1 h, and the spectra were measured under an NH_3(300 ppm)/He flow (100 $cm^3\,min^{-1}$) at 300 °C by accumulating 20 scans at a resolution of 4 cm^{-1}. A reference spectrum of WO_3/ZrO_2 was taken in flowing He, and was subtracted from each spectrum. The amount of adsorbed species was estimated from the integration of the IR bands on the basis of Lambert-Beer equation by using the extinction coefficient in the same way as described earlier [26].

2.3. Sensor setup and performances

Sensing characteristics were evaluated by using a conventional gas-flow apparatus equipped with a furnace operating at 200–500 °C. The sample gases containing various concentrations of NO_2 and NO were prepared by diluting a parent dry gas with base gas (typically 10% O_2 in N_2 balance). A schematic sensor element setup is shown in our previous paper [25]. Interdigital electrodes (Au) formed on the top of an alumina substrate were covered with a metal oxide electrolyte thick film as a sensing material. The alumina substrate covered with the sensing material was calcined at 600 °C for 1 h in air and assembled in a stainless flow cell. The sensor was exposed to the flow gas containing 10–1300 ppm of NO or NO_2, 1–99% O_2, and 0 or 2.5% H_2O in N_2 as balance at a flow rate of 100 $cm^3\,min^{-1}$. The stainless flow cell was heated at operating temperatures. The alternating current at a frequency of 4 Hz was applied to the sensor and the change in impedance was measured.

3. Results and discussion

First, the complex-impedance measurements have been performed (from 1 MHz to 4 Hz) in the base gas mixture (10% O_2 in N_2 balance) and in the sample gas containing 1300 ppm NO and 10% O_2 in N_2 balance at 500 °C. Fig. 1 shows the complex-impedance plots (Nyquist plots) for the Pt-WO_3/TiO_2-based sensing devise under a voltage of 2.0 V. The plot in the base gas mixture is composed of a compressed semicircle in a high frequency region (from 1 MHz to 25 kHz) prolonged by a curved line in a lower frequency region (from 25 kHz to