

Development of Paper Exhaust Catalyst Material for Emission Control in Small Internal Combustion Engines

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ABSTRACT

We have investigated the catalytic performance of a porous-structured paper containing noble metal catalysts such as platinum (Pt) and rhodium (Rh) supported on a thermally stabilized alumina (Al_2O_3). The catalysts were prepared by the usual impregnation method first, and then introduced into the macro porous-structured paper as catalytic active sites during the papermaking process. When the resultant paper was calcined at 1000°C for 60 h, it showed similar catalytic performance compared with the original powder-like catalyst. Particularly, the paper containing freshly prepared catalyst showed superior performance than a paper containing a commercially available alumina as support material. A small sized honeycomb-like structure was successfully prepared by using the catalyst paper, and this clearly indicates that the paper is a promising catalytic material for controlling exhaust emissions from small engines.

INTRODUCTION

Most catalytic converters used to “clean” exhaust systems in automobiles and other internal combustion engines consists of an inert structure (usually cordierite or metal) on which a catalytic active phase is supported [1-4]. To be used as the main support material for applications in high temperature environment, the catalyst paper must have thermal stability at even high temperatures. Paper-like composites made from ceramic fibers with catalyst powder have previously been prepared for hydrogen production use, e.g. as a structured catalyst for the conversion of methanol to hydrogen using methanol steam reforming (MSR) [5, 6, 21]. The catalyst powder was found to partially occupy the macro pores of the composite paper and was effective in converting methanol to hydrogen. In the MSR process, temperature range of 200°C - 350°C are usually used but in high temperature combustion applications such as in small engines, temperatures of 600°C - 900°C are used and the thermal stability of the paper is required to maintain the catalytic performance at these temperatures. Therefore the improvement of

thermal stability of the paper is important in the development of paper-based catalytic converters. A possibility of improving the thermal stability of the paper is the addition of meso porous gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) as support material during the papermaking process. But gamma alumina undergoes rapid transformation into the stable alpha ($\alpha\text{-Al}_2\text{O}_3$) phase at high temperatures with low thermal stability and drastic decrease in the surface area and as a result the catalyst phase deteriorates [7-9]. Therefore to be used as the “catalyst powder” in the macro porous paper, suppressing the transformation of $\gamma\text{-Al}_2\text{O}_3$ to the $\alpha\text{-Al}_2\text{O}_3$ phase and preventing the degradation of the surface area of alumina are necessary. One method of suppressing the transformation to the α -phase and maintaining a significant surface area at high-temperatures is by the doping of different elements such as La, Pr, Ba into alumina [10-16] and another method is using Si either during the preparation of the support itself or by surface modifications of available alumina [17-20].

In this work, we have examined the thermal stability of a commercially available thermally stabilized alumina (doped with different elements) and a surface Si-modified alumina which was freshly prepared from boehmite sol. We have introduced the two types of alumina with noble metal catalyst into the macro pore area of a porous-structured paper during the papermaking process and the catalytic performance of the catalyst papers was evaluated.

EXPERIMENTAL

CATALYST POWDER PREPARATION

The surface modified alumina ($\text{SiO}_2\text{:Al}_2\text{O}_3$) was prepared using a boehmite sol. The solvents in the sol were removed by heating the sol under reduced atmosphere in a rotary evaporator. The obtained powder was kept overnight in an oven at 100°C and then calcined at 600°C for 4 h. X-ray diffraction pattern of the resultant alumina showed the presence of $\gamma\text{-Al}_2\text{O}_3$ phase with surface area of about $178\text{ m}^2\text{g}^{-1}$. Silicon (Si) was introduced using tetraethoxysilane ($\text{Si}(\text{OC}_2\text{H}_5)_4$) (TEOS).

Wako Pure Chemical Industries, Japan) as precursor and the detailed preparation method has already been described [20]. The obtained solid was then dried in an oven at 100°C to remove adsorbed water and then calcined at 600°C for 4 h in flowing air. The SiO₂:Al₂O₃ samples were further calcined in air at 1000°C for 60 h and 1200°C for 4 h. Platinum (1 wt %) and rhodium (0.1 wt %) catalysts were loaded on the SiO₂:Al₂O₃ using the impregnation method. The catalyst precursors used were aqueous solutions of dinitro-diammine platinum, [Pt(NO₂)₂(NH₃)₂] and rhodium nitrate [Rh(NO₃)₃]. The solid powder obtained after impregnation was dried overnight in an oven at 100°C. The same amount of Pt and Rh (from Pt(NO₂)₂(NH₃)₂ and Rh(NO₃)₃) were impregnated with a commercial available thermal-stabilized alumina (Com-Al₂O₃), using the same experimental procedure above. The two support materials impregnated with Pt and Rh were then calcined in air at 600°C for 4 h and 1000°C for 60 h.

PAPER PREPARATION

These two catalysts supported on the different alumina were then introduced during the papermaking to produce porous-structured papers. The papermaking procedure for the fabrication of the porous-structured paper at the laboratory scale has been described in detail previously [5, 6, 21].

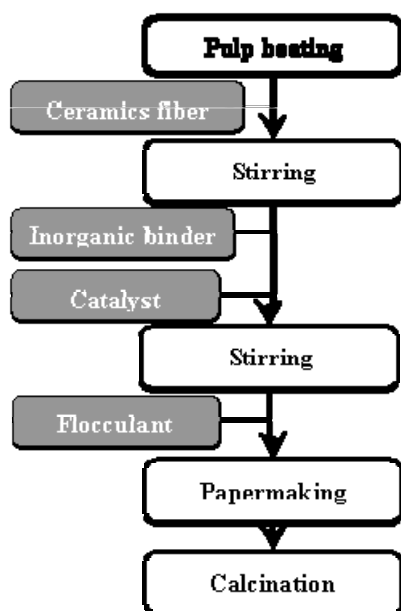


Fig.1 Outline for the preparation of catalyst paper

As shown in Figure 1, briefly, ceramic and pulp fiber in an aqueous suspension containing the catalyst powders were mixed with some additives and stirred. Flocculants used as retention aids were then added to the suspension and sheets of catalyst paper prepared according to the Technical Association of the Pulp and Paper Industry (TAPPI) standards [22]. The catalyst

paper obtained was dried and several pieces were made (1.5 cm x 5 cm) before calcining in air at 1000°C for 60 h.

CHARACTERIZATION OF CATALYST POWDER

X-ray diffraction analysis on the SiO₂:Al₂O₃ support was performed using Cu-K α radiation at 40 KV and 40 mA (Rigaku RINT2000, Japan) to observe the phase transformations at different calcination temperatures. Specific surface areas of the calcined samples were determined by the BET method using high purity nitrogen gas with an ASAP 2020 (Micromeritics, U.S.A.) after degassing in vacuum. The α -phase transformation temperature was determined by Thermogravimetric and differential thermal analysis (TG-DTA) performed at a heating rate of 10°C min⁻¹ in air from room temperature to 1500°C using a Thermos Plus TG 8120 system (Rigaku, Japan). The transformation temperature to the α -Al₂O₃ phase was obtained from the maximum peak of the differential thermal analysis (DTA) curve. To measure the mean size of the noble metals on the two support materials after calcination, a CO-pulse system, (Catalyst Analyzer, Bell Japan Inc) was used. The catalyst is first treated in oxygen at 400°C for 15 min followed by purging with He for 15 min, and then reduced in a flow of H₂ at 400°C followed by a purge with He for 15 min, then the catalyst is cooled down to 50°C in a flow of He and a series of CO pulses are injected until the amount of CO pulses reaches a steady state. The pore size distribution of the porous paper was characterized by mercury porosimetry PoreMaster 33P (Yuasa Ionics, Japan).

CATALYTIC PERFORMANCE

Catalytic performance of the catalyst powder and paper calcined at 1000°C for 60 h were determined by the conversions of carbon monoxide (CO), n-propane (C₃H₈) and nitrogen oxides (NO_x) with nitrogen balance as a function of catalyst temperature using test gas mixtures simulating the real exhaust gas composition. The light-off was determined as the temperature of 50% hydrocarbon (HC) conversion, which is used to indicate the efficiency of an automotive exhaust gas catalyst (the lower the light-off temperature, the more active is the catalyst). The experimental set-up for the catalytic measurement is shown in Figure 2. In this set-up, two different size reactors were used for the catalyst powder and paper. Measurements were carried out at atmospheric pressure using fixed steel bed reactor system equipped with mass flow controllers. The direction of gas flow during catalyst paper measurement is parallel to the plane of the paper as shown in Figure 2. During measurements, the temperature of the catalyst powder and paper were raised from room temperature to 600 °C and the gasses exiting the reactors were analyzed using Infrared gas analyzer (Yokogawa IR400). The total gas flow during the experiment was kept constant at 1000 ml/min corresponding to a gas hourly space velocity (GHSV) of 120000 h⁻¹ in the case of catalyst powder (volume used 5 ml) and a GHSV of