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NO_X reduction over paper-structured fiber composites impregnated with Pt/Al_2O_3 catalyst for exhaust gas purification

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Abstract Pt/Al_2O_3 catalyst powder was successfully incorporated in a microstructured paper-like matrix composed of a ceramic fiber network, by use of a simple papermaking technique. As-prepared composite, denoted paper-structured catalyst, was applied to the reduction of nitrogen oxide (NO_X) in the presence of propene, for exhaust gas purification. The paper-structured catalyst demonstrated higher NO_X reduction efficiency and more rapid thermal responsiveness than a conventional Pt-loaded honeycomb catalyst, indicating that the paper-like structure with interconnected pore spaces contributes to effective transport of heat and reactants to the catalyst surfaces. Furthermore, the paper-structured catalyst with the appearance of flexible paperboard has a high degree of utility. The efficiency of utilization of Pt catalyst was improved by using hierarchically assembled paper-structured catalysts with preferential location of Pt catalyst in the upper part. The paper-structured catalyst composite with paper-like utility and porous microstructure is thought to be a promising catalytic material for efficient NO_X gas purification.

Introduction

Exhaust gas from plant boilers and vehicles has been identified as one of the main sources of urban air pollution, and efficient purification of such pollutant gas is essential for environmental cleanup and protection [1, 2]. The three major pollutants in exhaust gases are considered to be hydrocarbons (HC) including methane (CH_4) and propene (C_3H_6), carbon monoxide (CO), and nitrogen oxide (NO_X) [2, 3]. At the present time, three-way catalytic converters containing noble metal catalysts such as Pt, Pd, and Rh are widely used for effective, simultaneous reduction of CO, HC, and NO_X [3, 4]. However, these noble metals are high cost and resources are limited, and it is important to use these materials as efficiently as possible.

A great deal of effort has been directed toward research and development of new catalytic materials with the aim of achieving low cost, energy conservation, and high performance with small amounts of noble metals [5–7]. One of the promising approaches is structural design of catalyst supports. In particular, structured catalysts that can promote effective diffusion of heat and reactants have been energetically developed [8]. In recent years, monolithic ceramic supports with honeycomb structure consisting of regularly arranged parallel channels have been popularized, especially as NO_X purification catalysts, due to their low pressure drop and large relative surface area [9, 10]. However, honeycomb-structured catalysts have the disadvantages of heaviness, poor lateral gas diffusion, and low thermal conductivity [11]. Hence, there is a need for novel structured catalysts for efficient gas purification, and various structured catalysts, e.g., foam [12] and wire-mesh [13], have been actively developed.

In continuous flow-type catalytic processes including exhaust gas purification, the thermal environment, and

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reactant distribution in the catalyst layer are considered to be inhomogeneous [14–16]. For that reason, it is essential for efficient catalyst usage to arrange the catalyst components in a manner such that their effectiveness is maximized. Thus, one of the present challenges is to optimize the distribution of catalytically active material in the catalyst layer [17]. However, conventional catalytic materials such as catalyst powders, pellets, and monolithic honeycombs present considerable difficulties in tailoring the catalyst arrangement.

In our previous studies, Pt catalysts such as Pt/Al_2O_3 powder and Pt nanoparticles supported on carbon fibers were successfully incorporated in a microstructured paper matrix with layered ceramic fiber networks, by means of a high speed, low cost papermaking technique [18, 19]. As-prepared paper-like catalyst/ceramic fiber composites, denoted paper-structured catalysts, were easy to fabricate and easily handled, and showed excellent conversion of NO to N_2 in the presence of CH_4. It was suggested that the paper-like structure, with interconnected pore spaces formed by the fiber network, may provide a favorable reaction environment to promote desirable gas diffusion within the catalyst layer. The paper-structured composite catalysts have the appearance of paperboard, and are vertically stackable on top of one another. Consequently the catalyst density is easily controllable in the laminate direction by use of a paper-structured catalyst support with variable content of catalytically active material. This is a unique feature that can open a new avenue for tailoring the catalyst arrangement to optimize catalyst operation.

In the present study, the catalytic performance of the Pt/Al_2O_3 powder-containing paper-structured catalyst has been compared with the performance of Pt/Al_2O_3 powder, pellets, a monolithic Pt-loaded honeycomb and a catalyst powder/ceramic fiber mixture, for catalytic reduction of NO_X in the presence of C_3H_6. In addition, the distribution of Pt was controlled in the laminate direction by taking advantage of the utility of the paper-structured catalyst. The effect of a gradient of catalytically active material in the gas flow direction on NO_X reduction was investigated to most efficiently utilize the Pt.

Experimental

Materials

Commercial Pt/Al_2O_3 catalyst powder, pellets (with 1 wt% Pt content) and a ceramic honeycomb-structured catalyst (400 channels/square inch, 5.6×10^3 mm^3/piece, Pt content 750 g m^{-3}) were purchased from Tanaka Kikinzoku Kogyo Co., Ltd. Ceramic fibers (IBIWOOL; 52 wt% SiO_2, 48 wt% Al_2O_3; IBIDEN Co., Ltd.) were washed with water and cut to average length 0.5 mm with a blender. Pulp fibers as a temporary supporting matrix in the papermaking process were obtained by refining commercial bleached hardwood kraft pulp (>90% *Eucalyptus grandis* natural hybrids, Brazil) to a Canadian Standard Freeness of 300 mL with a Technical Association of the Pulp and Paper Industry standard beater. Two types of flocculants were used for paper fabrication, namely cationic polydiallyldimethylammonium chloride (PDADMAC; molecular weight ca. 3×10^5 g mol^{-1}, charge density 5.5 meq g^{-1}; Aldrich Co., Ltd.) and anionic polyacrylamide (A-PAM, HH-351; molecular weight ca. 4×10^6 g mol^{-1}, charge density 0.64 meq g^{-1}; Kurita Co., Ltd.). Alumina sol (Snowtex 520, Nissan Chemicals Co., Ltd.) was used as a binder to improve the physical strength of the paper composites after calcination.

Preparation of paper-structured catalyst by a papermaking technique

The preparation of paper composites using organic and inorganic fibers and a dual polyelectrolyte retention system has been described in detail in our previous reports [18–22]. In summary, a water suspension of ceramic fibers and Pt/Al_2O_3 catalyst powder was mixed with PDADMAC (0.5 wt% of total solids), alumina sol binder, and A-PAM (0.5 wt% of total solids) in that order. The mixture was added to pulp fiber suspension, and solidified by dewatering using a 200 mesh wire. The wet handsheets were pressed at 350 kPa for 3 min, then oven dried at 105 °C for 1 h. The paper composites thus obtained were calcined at 500 °C for 30 min to remove pulp fibers and to improve the physical strength by alumina binder sintering. A catalyst powder/ceramic fiber mixture having the same composition as the paper-structured catalyst after calcination was also prepared as a control, by freeze-drying the inorganic mixture without addition of pulp.

Characterization

The Pt content of the paper-structured catalyst was determined by atomic absorption spectrophotometry using a Shimadzu AA-6600F instrument: the concentration of Pt ions extracted from the samples with a 3:1 mixture of 36% hydrochloric acid and 69% nitric acid was measured. Surface examination of paper samples was conducted using a scanning electron microscope (SEM, JSM-5600, JEOL, Ltd.).

Catalytic performance test

NO_X reduction performance testing was conducted according to our previous reports [18, 19]. A schematic diagram of the reactor setup is shown in Fig. 1, and a typical

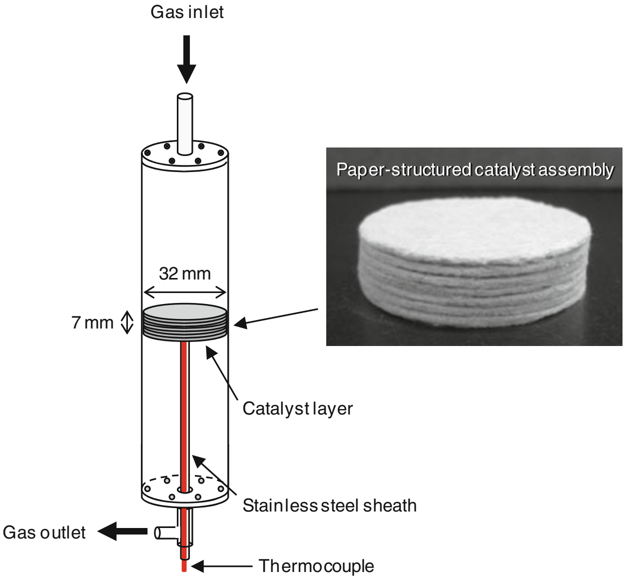


Fig. 1 Schematic diagram of a typical reactor setup

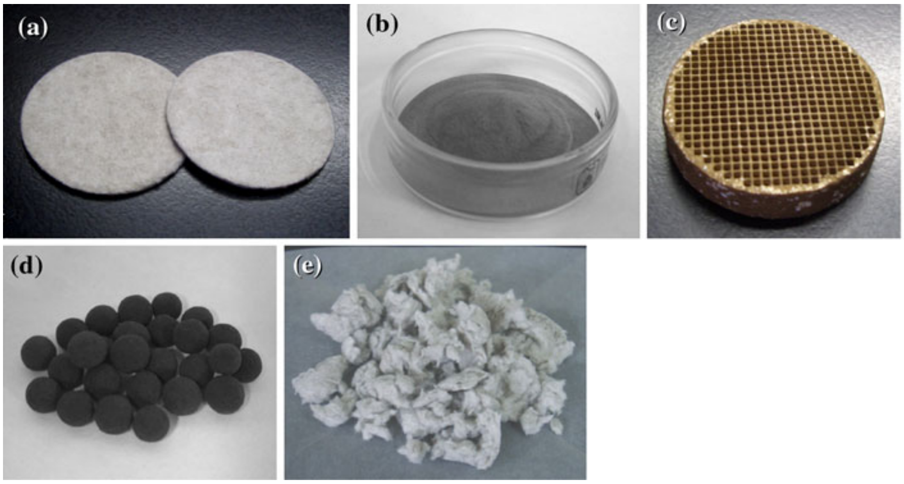
procedure was as follows. Seven circular pieces of the paper-structured catalyst, each with area 8.0 × 10^2 mm^2 and thickness 1.0 mm, were stacked vertically (5.6 × 10^3 mm^3). The cylindrical catalyst assembly (2.0 g, Pt 4.2 mg) was placed inside a stainless steel cylindrical reactor in which a ceramic fiber filter (QR-100, ADVANTEC, Ltd.) was set on the perforated support plate, in contact with the inner wall of the reactor. Commercial Pt/Al_2O_3 powder and pellets (0.42 g, Pt 4.2 mg) were mixed with ceramic powder (3.1 g) to adjust the total occupied volume to 5.6 × 10^3 mm^3 and packed in the cylinder. A monolithic honeycomb-structured catalyst (3.8 g, Pt 4.2 mg, 5.6 × 10^3 mm^3) was placed as is inside the reactor. In each case, the amount of Pt catalyst was maintained at 4.2 mg per test sample. The flow rates of gaseous reactants were regulated by mass flow controllers (Model 3660 or 3200 SR Series, Kofloc Co., Ltd.). A gas mixture composed of NO (400 ppm), C_3H_6 (892 ppm), O_2 (0.5%), and He (balance) was continuously passed through the packed catalyst samples at a constant flow rate of 5.0 × 10^5 mm^3 min^{-1} (gas space velocity 5,357 h^{-1}) at atmospheric pressure. The pressure drop during the catalytic reaction was monitored on line by a differential-pressure meter. The internal temperature of the reactor was controlled by a continuous heat supply system comprising a mantle heater and a thermocouple inserted in the catalyst layer. In the steady state, the gas composition during the catalytic reaction was monitored online using an NO_X analyzer (NOA-7000, Shimadzu Co., Ltd.). To elucidate the thermal responsiveness of catalyst samples, performance tests at elevated temperatures were also conducted at a heating rate of 2 °C min^{-1}.

Results and discussion

Paper-structured Pt/Al_2O_3 catalyst prepared by a papermaking technique

Figure 2 shows optical images of the catalyst samples that were used. The paper-structured catalysts with the appearance of flexible paperboard were lightweight (ca. 350 kg m^{-3}), easy to handle and easy to manufacture by the simple papermaking method, while commercial honeycomb catalysts are heavy (ca. 580 kg m^{-3}), and require a multistage manufacturing process. As we previously reported, the retention of inorganic materials including Pt/Al_2O_3 catalyst powder was more than 90% in the dual polyelectrolyte retention system [19]. Figure 3 shows SEM images of the surface of the paper-structured catalyst. The catalyst had an interconnected porous microstructure derived from the ceramic fiber network, in which Pt/Al_2O_3 powder was dispersed. The pore size was uniform and controlled (ca. 20 µm in diameter) and the porosity reached

Fig. 2 Optical images of **a** the paper-structured catalyst, **b** Pt/Al_2O_3 catalyst powder, **c** a Pt-loaded honeycomb catalyst, **d** Pt/Al_2O_3 catalyst pellets, and **e** a catalyst/fiber mixture



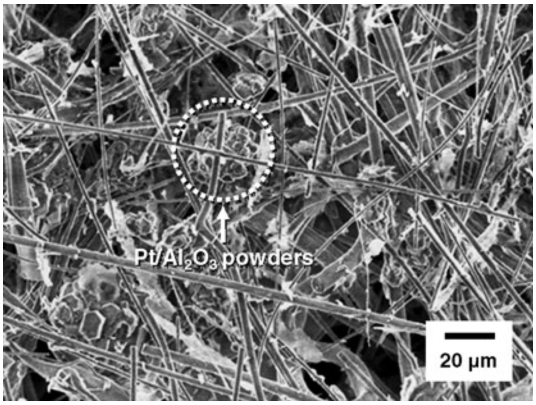


Fig. 3 SEM image of the surface of the paper-structured catalyst

ca. 70% [19]. Thus, a novel microstructured catalyst, i.e., a paper-structured composite catalyst, was successfully prepared by our well established papermaking technique.

NO_X reduction performance of paper-structured catalyst

The NO_X conversion efficiency from NO (as a model gas of NO_X) to N_2 of the paper-structured catalyst was compared with that of other catalyst samples. Figure 4 shows the steady state NO_X conversion behavior of the paper-structured catalyst, catalyst powder, a monolithic honeycomb catalyst, catalyst pellets, and a catalyst/fiber mixture. In each case Pt content and the occupied volume in the reactor were kept constant at 4.2 mg and 5.6×10^3 mm^3, respectively. The pressure drop during the catalytic reaction was significantly low (<1 kPa) in all test samples. Catalyst powder was highly active, but inconvenient to handle and thus impractical. Catalyst pellets were easily handled but had low activity, suggesting that accessibility of reactants to the catalytically active sites was limited to the outer surface of the pellets. By contrast, the paper-structured catalyst demonstrated both good practical utility and superb catalytic performance; the NO_X conversion efficiency of the paper-structured catalyst was comparable with that of the original catalyst powder. Interestingly, the paper-structured catalyst was far superior to a catalyst/fiber mixture, although both compositions were identical. We previously reported that a catalyst/fiber mixture had broader pore size distribution and larger interconnected pore spaces than the paper-structured catalyst [19, 20]. It was suggested that the regulated fiber-network microstructure with a uniform pore size of ca. 20 µm, which was formed inside the paper composites by our papermaking system [23], would contribute to the excellent catalytic performance of the paper-structured catalyst. In addition, the paper-structured catalyst showed superior catalytic performance to that of the commercial honeycomb-structured catalyst, indicating that the paper-like structure is more effective than the conventional honeycomb structure.

In practical applications, catalytic materials for exhaust gas purification are continually exposed to a large amount of heat transfer gases under heating and cooling conditions. Consequently, thermal responsiveness is one of the most important properties for ensuring acceptable catalytic performance under rapid temperature changes [13]. Figure 5 shows NO_X conversion behavior at elevated temperatures. Catalyst powder and pellets showed poor thermal responsiveness, suggesting that solid catalyst loading in the reactor caused localized gas flow in the catalyst layer and resulted in inefficient heat supply to the catalyst surfaces at elevated temperatures. On the other hand, the paper-structured catalyst and the honeycomb-structured catalyst displayed more rapid responsiveness to rapid temperature changes than did catalyst powder and pellets. The

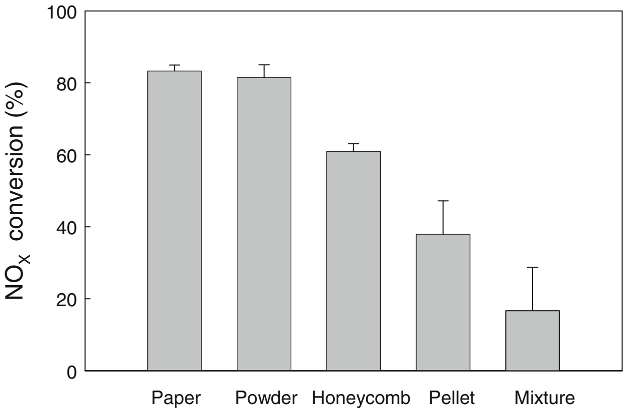


Fig. 4 NO_X conversion behavior of various catalysts in the steady state. Reaction temperature 230 °C. Pt content 4.2 mg/5.6×10^3 mm^3

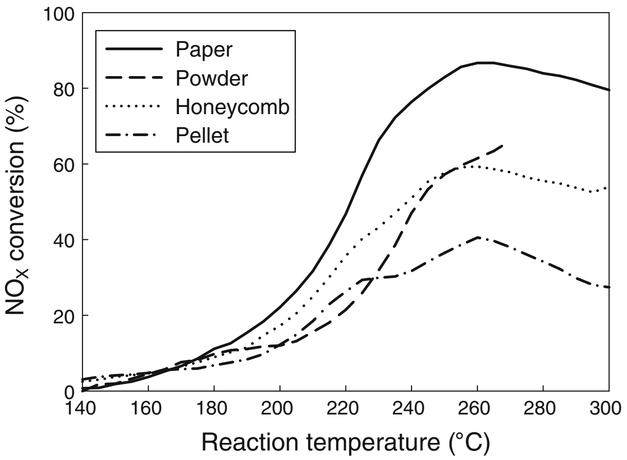


Fig. 5 NO_X conversion behavior of various catalysts heated at 2 °C min^{-1}. *Solid line*, paper-structured catalyst; *dashed line*, catalyst powder; *dotted line*, honeycomb-structured catalyst; *dashed-and-dotted line*, catalyst pellets. Pt content 4.2 mg/5.6×10^3 mm^3

implication is that the structured supports permit effective transfer of heat and reactants to catalytically active surfaces, and make the catalysts advantageous for rapid start-up and response to temperature changes. It should be noted that the paper-structured catalyst demonstrated superior thermal responsiveness compared with the honeycomb-structured catalyst. In general, honeycomb-structured catalysts composed of regularly arranged parallel channels suffer from poor sideways gas diffusion, despite smooth gas flow through the channels [11]. By contrast, the paper-structured catalyst allowed relatively isotropic gas diffusion in the interconnected pore spaces derived from the fiber network (Fig. 3), hence the catalytically active sites were readily accessible to gases. In our previous reports, the paper-structured catalyst demonstrated high conversion efficiencies of both NO_X and HC as compared with catalyst powder and honeycomb-structured catalysts, indicating that the paper-structured catalyst is effective for the simultaneous removal of NO_X and HC [18, 24]. On the basis of these results, it is suggested that the paper-like microstructure contributed to providing a suitable catalytic reaction environment and excellent catalytic performance, possibly by promoting efficient diffusion of heat and reactants. Such microstructural effects have been confirmed for other chemical reactions such as methanol reforming [16, 20–23, 25] and CO oxidation [26]. Thus, the paper-structured catalyst is regarded as a useful catalytic material for improving thermal responsiveness and gas purification efficiency.

Effect of catalyst gradient on NO_X reduction behavior

One of the promising approaches for efficient catalyst usage is to optimize the distribution of the catalytically active material in the catalyst layer [17]. Paper-structured catalysts with different Pt/Al_2O_3 content were hierarchically assembled to control catalyst density in the laminate direction, and the effect of Pt gradient in the gas-flow direction on NO_X reduction behavior was investigated. As shown in Fig. 6, we constructed three models to determine which part of the catalyst layer is more effective. In each model, ceramic fiber filters were used to clarify differences in the catalyst gradient. Figures 7 and 8 show NO_X conversion in the steady state and at elevated temperatures, respectively. Sample 2 gave the best catalytic performance, indicating that the upper part of the catalyst layer is more important for efficient NO_X conversion. The precise mechanism of NO_X reduction with C_3H_6 is still not fully understood. However, it is considered to be the combination of exothermic C_3H_6 oxidation ($C_3H_6 + 9/2O_2 \rightarrow 3CO_2 + 3H_2O$) and endothermic NO_X reduction ($9NO + C_3H_6 \rightarrow 9/2N_2 + 3CO_2 + 3H_2O$) [27]. Since C_3H_6 oxidation is faster than NO_X reduction, reaction heat is generated mostly at the reactor entrance, whereas heat consumption occurs in the middle and bottom of the reactor. From this point of view, it is suggested that the excellent performance of sample 2 was due to most of the Pt being located in the upper part of the catalyst layer where the temperature was relatively high, favoring the endothermic NO_X reduction reaction.

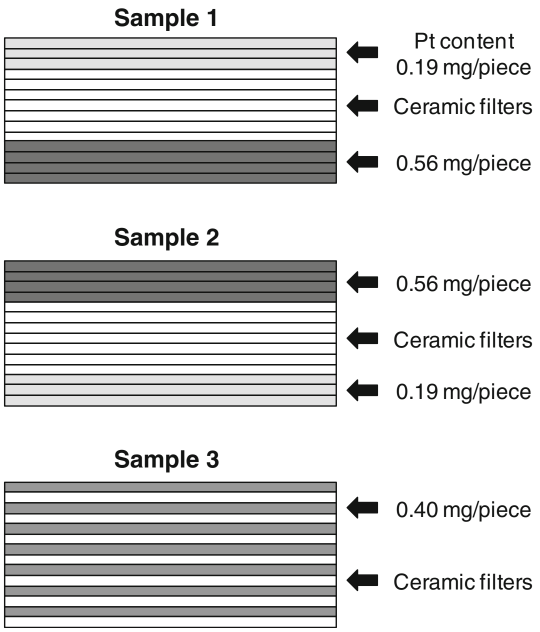


Fig. 6 Schematic cross-sectional diagrams of three catalyst gradient models using paper-structured catalysts with different Pt content. Total Pt content of each model is 2.8 mg/11.2 × 10^3 mm^3

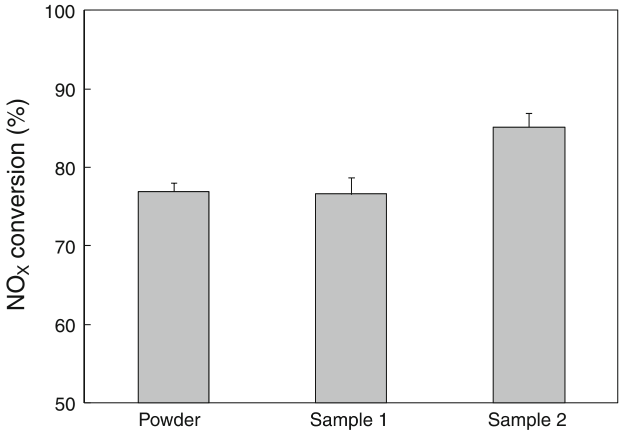


Fig. 7 NO_X conversion in the steady state. Reaction temperature 280 °C; Pt content 2.8 mg/11.2 × 10^3 mm^3. Catalyst powder was packed normally into the reactor

Subsequently, reduction of Pt usage was investigated (Fig. 9). Samples 4 and 5 were similar models to samples 1 and 2, respectively, except that the Pt content was 25% smaller (2.1 mg). In the case of catalyst powder, the Pt content was set at 2.8 mg. While the NO_X conversion

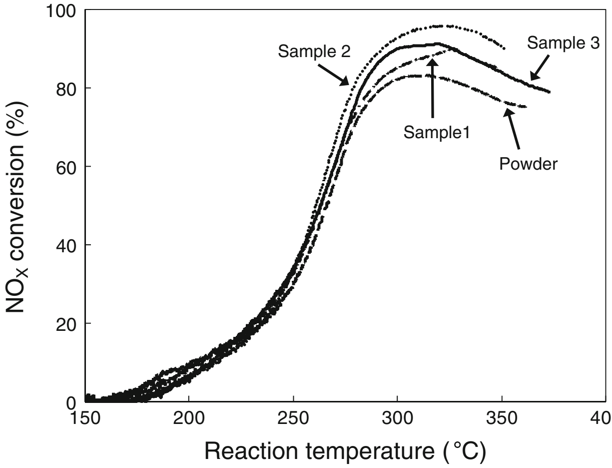


Fig. 8 NO_X conversion during heating at 2 °C min^{-1}. Pt content 2.8 mg/11.2 × 10^3 mm^3. Catalyst powder was packed normally in the reactor

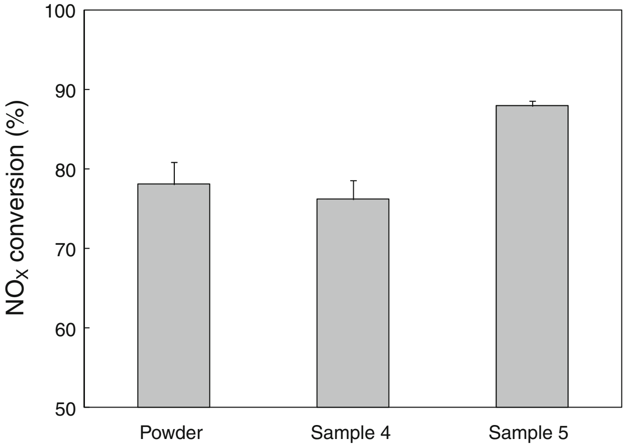


Fig. 9 NO_X conversion behavior in the steady state. Reaction temperature 300 °C. Pt content 2.8 mg/11.2 × 10^3 mm^3 (powder) or 2.1 mg/11.2 × 10^3 mm^3 (samples 4 and 5). Samples 4 and 5 are similar models to samples 1 and 2, respectively, except for Pt content

efficiency of sample 4 was slightly lower than that of the catalyst powder, sample 5 demonstrated much higher NO_X conversion efficiency than the catalyst powder even though the Pt content of sample 5 was 25% lower than that of the catalyst powder. These results suggest that assembly of the paper-structured catalysts with the Pt located preferentially in the upper part, can reduce Pt usage by more than 25% compared with the case of simple packing of catalyst powder. The paper-structured catalyst has a high degree of utility as well as excellent catalytic performance, and allows for a versatile configuration design, e.g., corrugated board forms and further processing [24]. Thus, there would be much interest in further research and development of the paper-structured catalyst for efficient catalyst utilization.

Conclusions

Paper-structured Pt/Al_2O_3 catalyst composites with ceramic fiber network microstructure were successfully prepared by a simple papermaking technique. In the NO_X reduction process for exhaust gas purification, the paper-structured catalyst demonstrated high catalytic efficiency and rapid thermal responsiveness compared with the original catalyst powder and the conventional honeycomb-structured catalyst. It is suggested that the well-controlled fiber-network microstructure with connected pore spaces inside the paper-structured catalyst provides a suitable catalytic reaction environment by promoting gas accessibility to the catalyst surfaces. In addition, the catalytic performance of the paper-structured catalyst improved with preferential location of Pt/Al_2O_3 in the upper part of the catalyst layer, leading to reduction of Pt usage by more than 25% compared with the case of simple packing of catalyst powder. This concept for efficient catalyst usage will break new ground in catalyst engineering fields, and the paper-structured catalyst with paper-like utility and porous microstructure is expected to be an advanced catalytic material for efficient gas purification.

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