Reaction Characteristics of Monolithic Catalysts with Different Size of Channels for NO_x Reduction

By

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Abstract

The NO_x reduction with carbon and NH_3 on various monolithic catalysts was investigated over a wide range of space velocity. A three-component composite catalyst, Co-La_2O_3-Pt, supported on active carbon (DIAHOPE 008) was used. It was pulverized into fine powder, and after mixing with hydrogel of aluminum hydroxide, this was molded into cylindrical forms with an inner channel of three sizes along the axial direction. The maximum limit of space velocity (SV_{max}) to achieve a 100% NO conversion was mainly discussed. The same catalyst components were extensively supported on substrates having various channel structures of ceramic honeycomb. For these substrates, the effects of alumina sol-precoating and thermal treatment on the NO-NH_3 reaction were studied. The 0.93% Co-0.51% La_2O_3-1.6% Pt catalyst supported on the honeycomb precoated with 9.2% Al_2O_3 and calcined at 600°C for 1 hour gave the best performance among the various catalyst components. It also showed the best performance among the various structures from the viewpoint of SV_{max} for achieving a 100% NO conversion.

1. Introduction

In our previous work, it was reported that composite catalysts composed of iron group metals, rare earth oxides and platinum group metals such as Co-La_2O_3-Pt and Fe-La_2O_3-Pt were found to be active for the reduction of NO with active carbon$^{1)}$ or $NH_3$$^{2)}$. Since one of the main objectives in these studies was to elucidate the relationships between catalyst components and their activities, small particles (30-40 mesh) were used without consideration for practical use. In practice however, in order to avoid a large back-pressure, a monolithic catalyst such as a ceramic honeycomb which has straight channels is used for NO_x-containing exhaust gas with a high space velocity$^{3\sim5)}$. There have been few studies in the field of dynamic performance of these catalysts, apart from studying a variety of reaction mechanisms or mathematical analysis$^{6)}$.

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In this study, in order to clarify the basic characteristics of the catalysts having blow-by structure, the active carbon supported catalyst in particle form was crushed into powder and molded into a cylindrical shape with an inner channel of three different sizes. This was to be regarded as the unit cell of a honeycomb structure. The reactions of NO-C and NO-NH_3 on these catalysts were investigated at high space velocities. When the catalyst was to be supported on a honeycomb structure, various methods of sol-coating prior to the catalyst impregnation were investigated to increase the surface for the dispersion of catalyst particles.

2. Experimental

2. 1. Catalyst

An active carbon, DIAHOPE 008, produced by the Mitsubishi Chemicals Co. Ltd. was used as the catalyst support. It was 40-60 mesh in size, and had a BET-surface area of 1200 $m^2\ g^{-1}$, a bulk density of 0. 42 g cm^{-3}, and a porosity of 0. 34 $cm^3\ cm^{-3}$. A catalyst was prepared by the following impregnation method. Platinum was first dispersed in the reduced metallic state on the support, and then cobalt and lanthanum oxide were supported together[7]. The prepared catalyst, 5. 0% Co-2. 7% La_2O_3-0. 70 % Pt, was milled for one hour by a dry method, and for an additional hour by a wet method. A block diagram of preparing a cylindrical shape with an inner channel

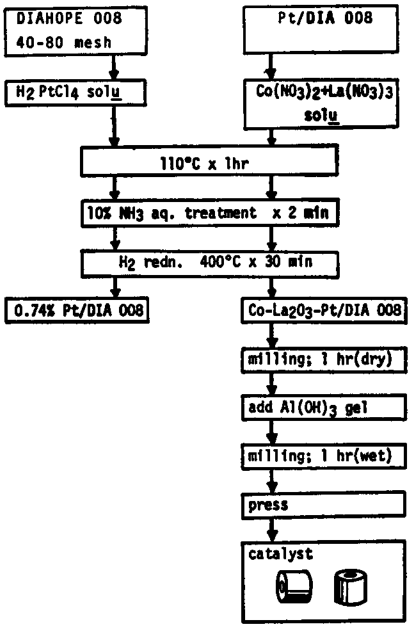


Fig. 1 A block diagram of preparing cylindrical catalysts with inner channel.

is shown in Fig. 1. The prepared catalyst, after milling, was molded into a cylindrical shape of 8.5 mm o.d. with an inner channel of three sizes: 2.5, 3.6 and 4.4 mmϕ, which were designated as S, M and L, respectively. The length of each piece was 7.0 mm. Aluminum hydroxide gel prepared from $Al(NO_3)_3$ and ammonia solutions was added as a binder before the wet milling, 17wt% as a dry base. These cylindrical catalysts were crushed into 40-60 mesh granule for comparison. In addition, two kinds of ceramic honeycomb were used for comparison. This was made by the Nippon Tokushu-ki Kogyo Co. Ltd. and the composition was cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$). One had triangular cell cross sections (pitch: 2.10 mm, cell density: 52.4 cm^{-2}) and the other had sguare cell cross sections (pitch: 1.50 mm, cell density: 28.0 cm^{-2}). Since these honeycombs had small BET-surface areas (0.53 $m^2 g^{-1}$), Al_2O_3- or SiO_2-sol was precoated by various methods. A honeycomb support was dipped into 10% of alumina-sol or 30% of Cataloid (silica-sol) prepared by the Nissan Chemicals Co. Ltd., and the excess was separated by centrifuging the support at 2000 rpm. The sol-pretreatment was conducted repeatedly up to six times to obtain a support with a 2-10 wt% Al_2O_3- or SiO_2-loading when dried. The Al_2O_3- or SiO_2-precoated support was immersed in an impregnating aqueous solution of chloride or nitrate salts with concentrations of 17 or 35 wt%. It was then put in the centrifuge (2000 rpm) for 30 sec, followed by the same treatment as for the active carbon supported catalyst. Calcination at 600°C for 1 hour was also conducted after the sol-precoating.

2.2 Reaction operation

A continuous flow reaction apparatus was operated under atmospheric pressure. One to eight pieces of each cylindrical catalyst were packed in a quartz tube with an inner diameter of 8.5 mm. A pyrex glass capillary tube of the same inner and outer diameters as the cylindrical catalyst was placed at both ends of the catalyst bed. By this device the reaction gas contacted exclusively with the inner wall of the catalysts. The void between the outer surface of the honeycomb catalyst and the inner wall of the reaction tube was filled with asbestos. The temerature was maintained by a tubular electric furnace of 700 mm length. A thermocouple was located at the end of the catalyst bed. Temperature distribution was uniform for 70 mm length within ±2°C even under a N_2 flow of 8500 $cm^3 min^{-1}$ at about 300°C. The temperature was raised by a heating rate of 3°C min^{-1} to the reaction temperature. Gas compositions were 0.2% NO for the NO-C reaction and 0.1% NO-0.1% NH_3 for the NO-NH_3 reaction. Nitrogen was the diluent. The flow rate was varied from 13 to 8330 $cm^3 min^{-1}$. The effluent gas was analyzed by a gas chromatograph with columns of Porapak Q for N_2O and CO_2, MS-5A for O_2, NO and CO, and Porapak T for NH_3. The pressure drop for the catalyst bed of 56 mm length against a high space velocity of N_2 was measured at 20°C by a water manometer.

3. Results and Discussion

3.1. Back pressure measurement for various catalysts

The pressure drop of each support, ΔP in Torr cm^{-1}, at 20°C under the N_2 flow is shown in Fig. 2. The cylindrical supports had very small values of ΔP, which was 1/30-1/100 of the value for the granular support. The honeycomb had the lowest ΔP value of all.

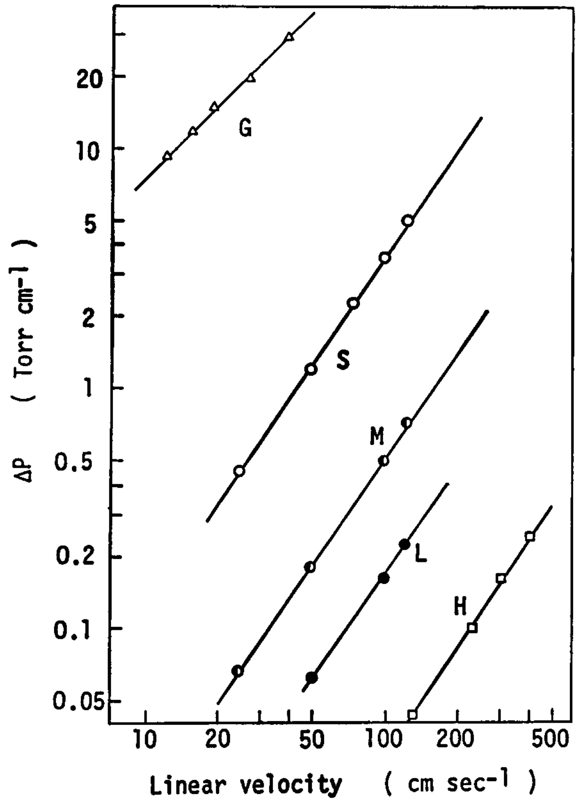


Fig. 2 Back pressure for various supports against different linear velocities. G : granule, H : honeycomb, S, M, L : cylinders with different channel diameters, ΔP (Torr cm^{-1}) $= a \times 10^{-4} (LV)^b LV$ (cm sec^{-1}). The values of the constants a and b in the ΔP equation were as follows; G: $a=7600$ $b=1.00$, S: $a=36$ $b=1.46$, M: $a=5.7$ $b=1.47$, L: $a=2.1$ $b=1.46$, H: $a=0.29$ $b=1.50$.

3.2. Performance of $NO\text{-}NH_3$ reaction on honeycomb catalysts prepared by different methods

The $NO\text{-}NH_3$ reaction on the honeycomb catalyst which was prepared without

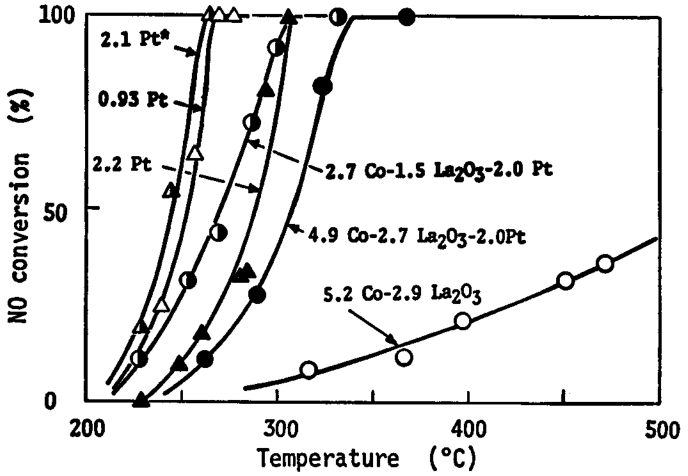


Fig. 3 Activities of the NO-NH_3 reaction on various catalysts supported on the honeycomb support triangular cell cross section without precoating. * : two-step supporting, 0.8% NO-1.5% NH_3 SV : 39600 h^{-1}.

precoating of sol was first investigated by varying the catalyst component and loading. As shown in Fig. 3, the 0.93% Pt catalyst was the most active among catalysts tested, and the activity increased slightly by depositing Pt twice, i. e. 2.1% Pt. However, the activity decreased when 2.2% Pt was impregnated in a single step by a concentrated H_2PtCl_6 solution. The apparent metal particle sizes of these Pt catalysts were estimated from the amount of CO adsorbed at room temperature, i. e. 20.9, 30.8 and 42.1 nm for 0.93% Pt, 2.1% Pt (twice) and 2.2% Pt (once), respectively. The ratio of the number of CO adsorption sites is 1 : 1.53 : 1.17 in the same order. Furthermore, a synergistic effect on the reaction rate, which was commonly observed in the NO-NH_3 reaction on the active-carbon supported catalysts[2] was not observed when the Co-La_2O_3 components were added. These non-enhanced activities must be attributed to the small surface area (0.53 m^2 g^{-1}) of the honeycomb support.

When the honeycomb support was pre-coated with Al_2O_3 or SiO_2, the catalysts exhibited a high activity for the NO-NH_3 reaction, as shown in Fig. 4. A synergistic effect was observed on the composite Co-La_2O_3-Pt catalyst. Alumina sol coating caused a better performance than SiO_2 sol coating, and the catalyst activity increased with the increase of Al_2O_3 loading.

Other treatments of precoated support were extensively studied, and the results are shown in Fig. 5. The NH_4Cl treated support after an Al_2O_3 pre-coating made a Pt deposit only on the outer surface of the support, which produced a highly dispersed (5.2 nm) catalyst in comparison with others. Some form of ammine-complex was probably deposited. Another Al_2O_3 pre-coating method was investigated by treating

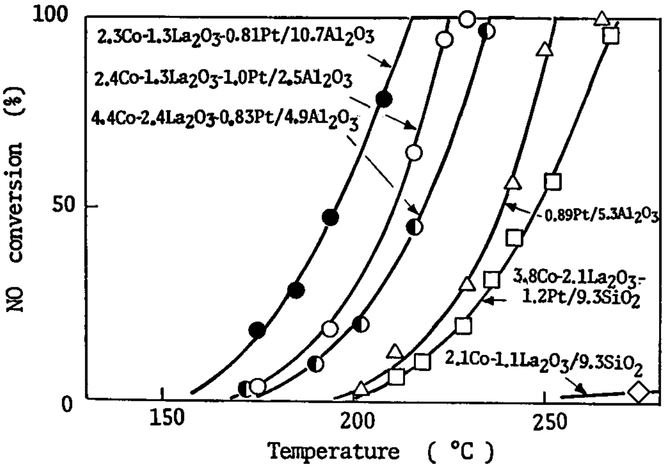


Fig. 4 Activities of the NO-NH_3 reaction on various catalysts supported on the honeycomb support (square cell cross section) with precoating of alumina sol. Reaction conditions were the same as noted in Fig. 3.

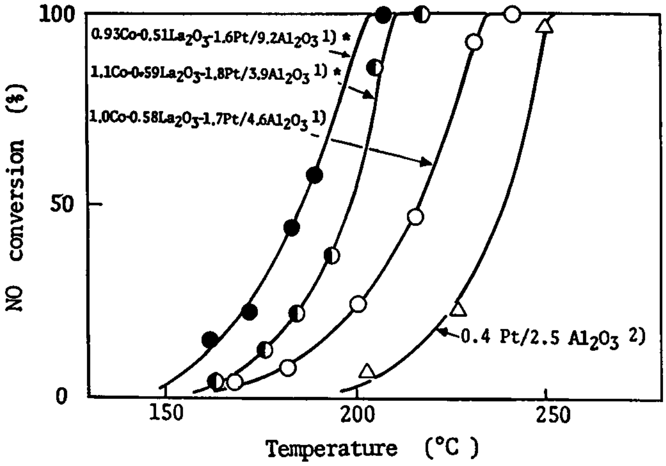
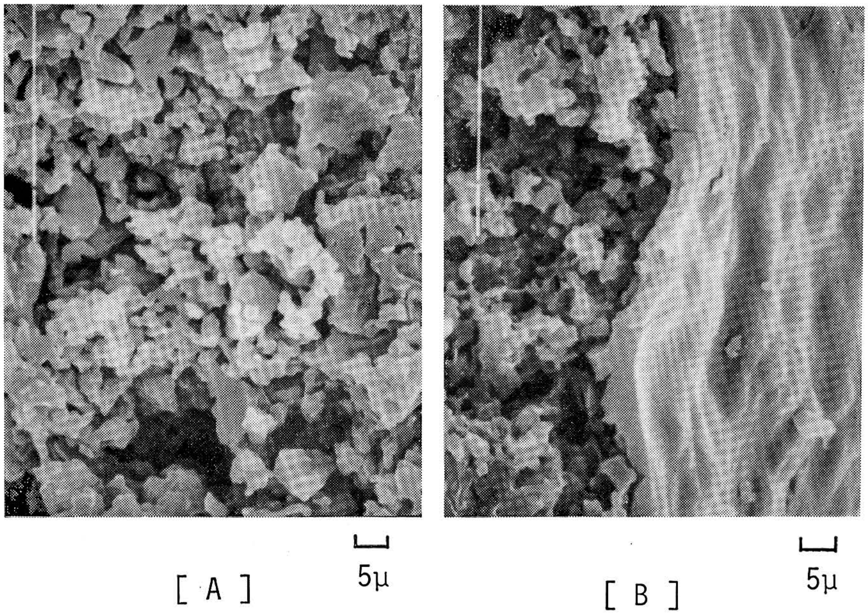


Fig. 5 Activities of the NO-NH_3 reaction on various catalysts supported on the honeycomb support (square cell cross section) precoated with alumina by different methods. 1) : Al $(NO_3)_3$-NH_3 method, 2) : Alumina sol-NH_4Cl method, * : precoated supports were treated at 600°C for 1 hour in an air stream, reaction conditions were the same as noted in Fig. 3.

an $Al(NO_3)_3$-coated honeycomb with NH_3 vapor, which produced a better catalyst performance than the Al_2O_3 sol pre-coating. Calcination at 600°C for 1 hour in flowing air was also effective. In the case of the alumina sol precoated support, the



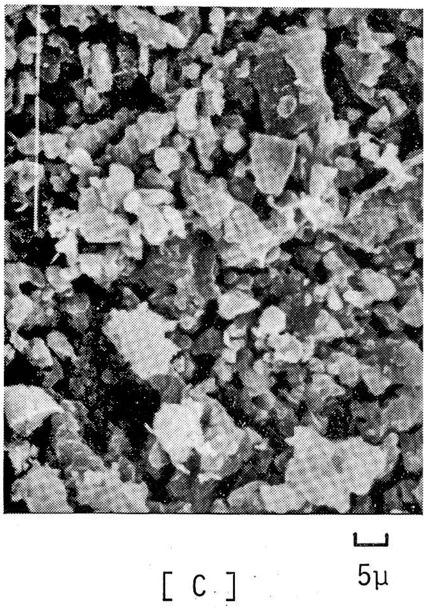


Fig. 6 SEM photographs of the honeycomb support with alumina-sol precoating. [A] : honeycomb support, [B] : alumina-sol precoating (11.0%), [C] : $Al(NO_3)_3$-NH_3 precoating (10.7% Al_2O_3).

coating layer was formed on the surface of the support, as shown in Fig. 6. Hawever, when the support was treated by $Al(NO_3)_3$-NH_3, Al_2O_3 was dispersed through the support.

As far as an optimal concentration of catalyst loading was concerned, the amount

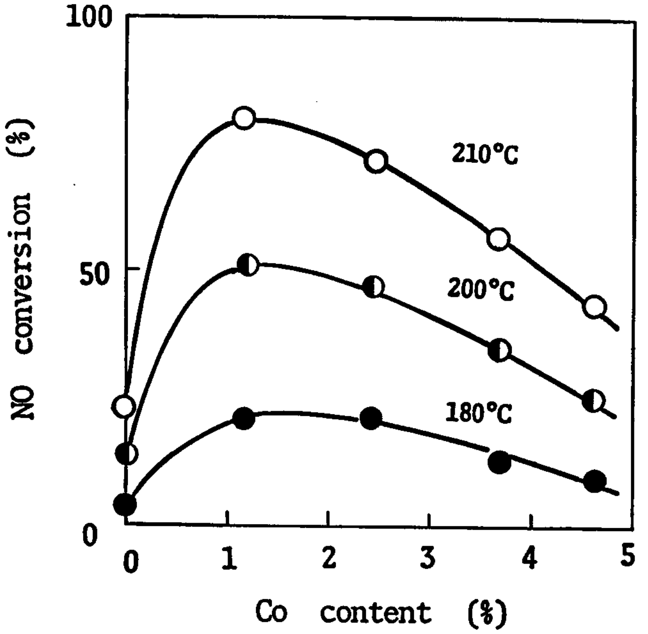


Fig. 7 Effect of Co loading on the activity. $Al(NO_3)_3$-NH_3 treated support, catalyst: Co-La_2O_3-0.80% Pt (Co/La atomic ratio=5). Honeycomb with square cell cross section.

of Co-La_2O_3 components in the Co-La_2O_3-Pt catalyst was varied, and the highest activity was obtained for about 1% Co-0.6% La_2O_3-0.8% Pt, as shown in Fig. 7.

3.3. Performance of cylindrical catalysts for the NO-NH_3 reaction

The NO-NH_3 reaction was investigated, using eight pieces of each cylindrical catalyst by varying the space velocity, and the results for catalyst S are shown in Fig. 8. The SV was calculated based on the reactor volume occupied by a catalyst: 3.18 cm^3. In order to obtain the temperature required for a 100% NO conversion, the temperature-conversion data in Fig. 8 were plotted on logarithmic coordinates. The linear relationships between the SV and NO conversion on logarithmic scales for each temperature data were obtained as shown in Fig. 9. A space velocity, which is given as an intersecting point on the 100% NO conversion level for each line, gives the maximum limit of space velocity (SV_{max}) for the 100% NO conversion at each temperature. In the same manner, SV_{max}'s for various levels of NO conversion were estimated and plotted in Fig. 10. SV_{max}'s for the 80% and 100% NO conversions were not much different between the catalysts S and M. However, for the lower NO conversion levels, SV_{max} for the catalyst having a smaller channel was larger than those of larger channels. This means that the blow-by is dominant at high SV

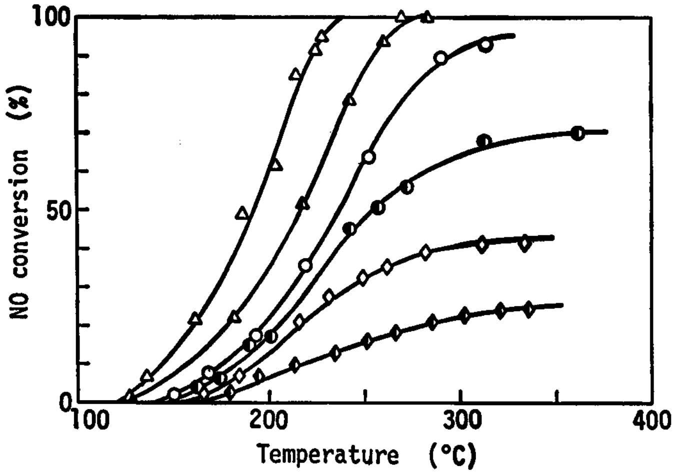


Fig. 8 Activities of the NO-NH$_3$ reaction on catalyst S at various space velocities. Catalyst: 4.2% Co-2.3% La$_2$O$_3$-0.58% Pt/12% Al$_2$O$_3$-DIAHOPE 008, reaction gas: 0.1 % NO-0.1% NH$_3$, balance N$_2$, SV (h^{-1}): △3800, ▲7900, ○15000, ◐32000, ◇72000, ◆98000.

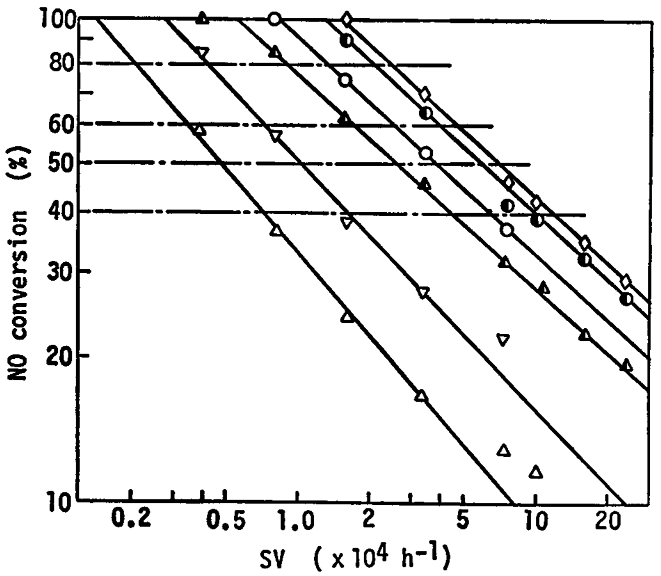


Fig. 9 NO conversion vs SV at various temperatures. Temperatures: △200°C, ▽220°C, ▲250°C, ○270°C, ◐300 °C, ◇350°C.

ranges, especially in a catalyst having a larger channel. However, since a certain residence time is necessary for a 100% NO conversion, the catalyst M showed the best performance, probably due to the balance between the negative effect of blow-by

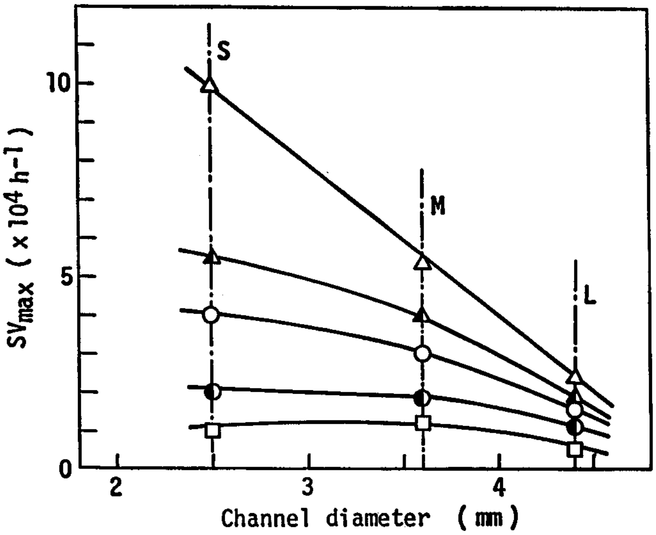


Fig. 10 SV_{max} for the three sizes of cylindrical catalyst, S, M, L, at various NO conversion levels. Temperature: 300°C, NO conversion: △40%, ▲50%, ○60%, ◐80%, □100 %.

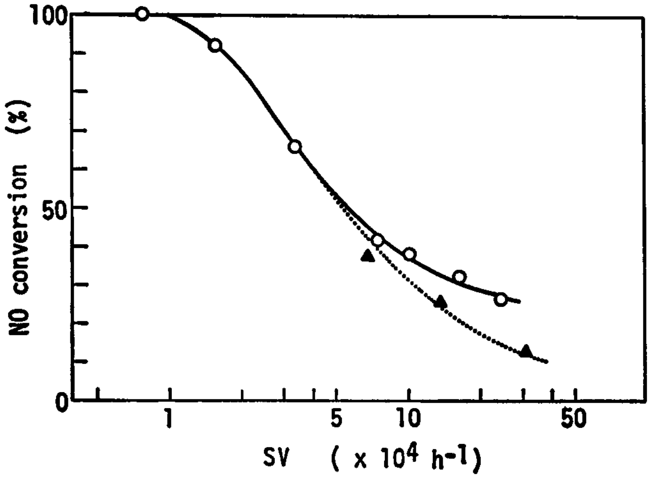


Fig. 11 Performance of the catalyst S in the high space velocity region. Reaction gas: 0.1% NO-0.1% NH_3, balance N_2 temperature: 300°C, solid line: LV was varied at a constant catalyst-bed length, dotted line: catalyst-bed length was varied at a constant LV.

and the positive effect of residence time. In the case of the catalyst S, the SV dependence of a NO conversion at a constant temperature was extensively investigated by varying the catalyst-bed length and linear velocity (LV). As shown in Fig. 11,

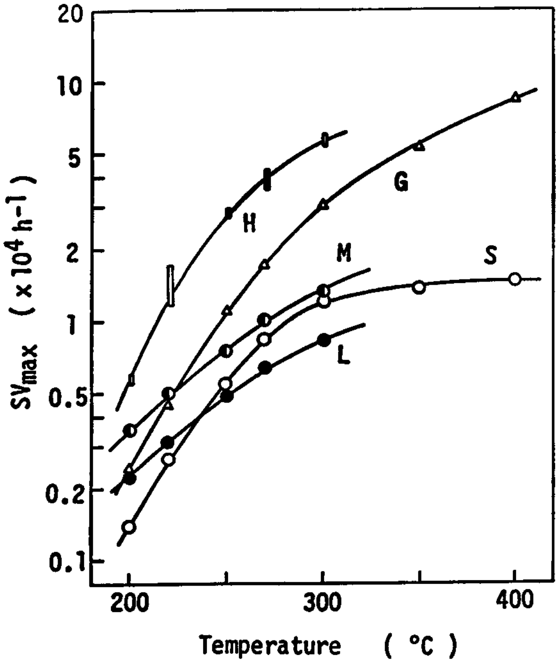


Fig. 12 SV_{max} for 100% NO conversion for different catalyst structures in the NO-NH_3 reaction. Reaction gas: 0.1% NO-0.1% NH_3, balance N_2 catalyst: 4.2% Co-2.3% La_2O_3-0.58% Pt/12% Al_2O_3-DIAHOPE 008 for G, S, M and L, 1.1% Co-0.62% La_2O_3-0.48% Pt/4.7 % Al_2O_3 for H.

higher NO conversions were obtained for higher LV's under the same SV condition. This difference is interpreted as a turbulency effect to increse the effective diffusion of the reaction gas through the gas film.

As far as the SV_{max} for a 100% NO conversion is concerned, performances of the various catalyst structures described in Fig. 2 were compared, and are shown in Fig. 12. Although the granular catalyst showed a better performance than the cylindrical catalysts, it had a high flow resistance at such operation conditions (2.3-119 Torr cm^{-1}). On the other hand, the 1.1% Co-0.62% La_2O_3-0.48% Pt catalyst supported on the honeycomb showed the best performance of any structure without a large back pressure. This is partly because that catalyst has a more complex channel matrix compared to the cylindrical structure.

3.4. The difference in SV dependence on the cylinder catalysts between the NO-C and NO-NH_3 reactions

The NO-C reaction was investigated, using one piece of each cylindrical catalyst by varying SV. The results for the three sizes of the catalysts (S, M, L) are shown

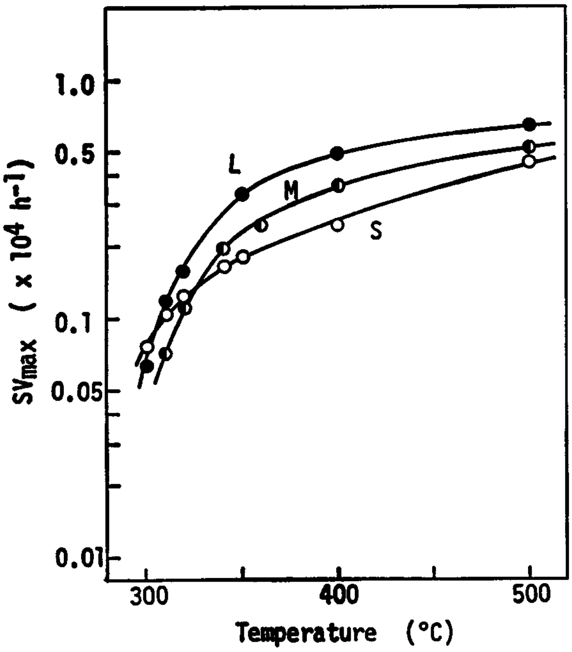


Fig. 13 SV_{max} for 100% NO conversion for each cylindrical catalyst in the NO-C reaction.

in Fig. 13 in the form of SV_{max} vs temperature, which was obtained in the same manner as in the NO-NH_3 reaction. Each catalyst sample was replaced by a new one after each reaction operation in order to avoid any effect of carbon consumption. The maximum carbon consumption after the reaction operation was 5.6%, and reproducibility of the data was ascertained by this sample. Apart from the facts that a higher temperature was needed and the SV_{max} value was relatively small compared to the NO-NH_3 reaction, the catalyst L showed the best performance, which was the opposite of the result in the NO-NH_3 reaction. Since the NO-C reaction consumes the carbon, the channel shape having the largest outer surface area was probably most favorable for this reaction under such lower SV_{max} values.

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