Research Report

NOx Selective Catalytic Reduction over Pt Supported Catalyst Promoted by Zeolite and CeO_2-ZrO_2

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HC吸着を利用した選択還元型NOx触媒

田辺稔貴，畑中美穂，辻龍介，新庄博文

Abstract

The emission control of NOx in exhaust gases is one of the greatest engineering challenges to extend the practical and commercial application of diesel and lean burn engines. One solution is selective NOx reduction using hydrocarbons in an oxidizing atmosphere. We mainly focused on catalytic reactions under temperature excursion because of the resemblance to conditions prevailing in real automotive exhaust. Adsorbed hydrocarbon on zeolite was found to be highly effective in reducing NOx at elevating temperature. Thus, we proposed a novel catalyst formulation involving zeolite and CeO_2-ZrO_2. Our catalyst concept consists of supported Pt on thermally stable oxides (such as SiO_2), zeolite and CeO_2-ZrO_2. Hydrocarbons adsorb on zeolite at low temperatures and migrate to the Pt surface at elevating temperature to reduce NOx. The active oxygen generated from CeO_2-ZrO_2 suppresses the poisoning effect of hydrocarbons at low temperature, promoting NOx reduction.

Keywords NOx, Reduction, Hydrocarbon, Adsorption, Platinum, Zeolite, CeO_2-ZrO_2

要　旨

ディーゼルエンジンやリーンバーンエンジンの利用範囲を広げていくためには，エンジン排気中のNOxを削減することが重要な課題の一つである。酸化雰囲気における炭化水素による選択的NOx還元反応はこの課題に対応する技術の一つである。我々はこの反応において、主に温度が時間とともに変化する過渡的な状態での触媒反応特性に注目して研究を行った。このような温度の過渡状態は現実の自動車排気において特に重要である。その結果，ゼオライトに吸着した炭化水素が昇温中において効率よくNOxを還元できることを見出した。この事実に基づいて，ゼオライトとCeO_2-ZrO_2添加による活性向上という新しいコンセプトの触媒構成を提案した。この触媒はシリカなどの耐熱性酸化物担体に担持された白金触媒，助触媒としてのゼオライトおよびCeO_2-ZrO_2から構成されている。ゼオライトに吸着した炭化水素は昇温過程において白金上へ移動しNOxを効率よく還元する。またCeO_2-ZrO_2から生成した活性酸素が吸着炭化水素による低温での吸着被毒を緩和する。

キーワード NOx，還元，炭化水素，吸着，白金，ゼオライト，CeO_2-ZrO_2

1. Introduction

Diesel and lean burn engines are superior to conventional Otto cycle engines with regard to fuel consumption. Thus, these engines have the potential of reducing CO_2 emission in automotive exhaust and help suppress Global Warming. In order to extend the commercial applications of these engines, the challenging problem of the emission control of NOx in exhaust gases has to be overcome.1, 2) NOx reduction in such an exhaust gas environment is very difficult because of the oxidizing atmosphere. Selective catalytic reduction with hydrocarbons (HC) is one of the techniques for NOx abatement in oxidizing atmosphere.2) Although Cu-ZSM-5 is well known to be a very active catalyst for this reaction,3-5) it does not have enough durability to be of any practical use.6, 7) Pt supported catalyst is known to be active at relatively low temperatures (473 - 673 K) and suitable for diesel engine exhaust applications.8-10) However, the catalyst's NOx reduction activity is not enough to be of practical use.

The automotive catalyst is usually used in non-steady state reaction conditions.11) The space velocity, concentration of reactants, and reaction temperature all vary with time. Thus, the activity of the catalyst under non-steady state conditions needs to be considered in addition to its steady-state behavior. This report addresses the importance of adsorbed hydrocarbon on catalysts for selective NOx reduction under temperature excursion and proposes a new concept for a catalyst specially designed for performance under such conditions.

2. Experimental methods

2. 1 Catalyst preparation and characterization

A pellet type catalyst was used. Catalysts were prepared by a conventional impregnation method. Pt was loaded on support material by impregnation of an aqueous solution of $Pt(NH_3)_2(NO_2)_2$ (Tanaka Kikinzoku Co.). After drying in an oven at 390K for 24 hours, the powder was calcined in flowing air at 773 K for 5 hours. The powder was compressed, crushed and then sieved to obtain catalyst pellets with a diameter of 0.50 - 0.75 mm. Pt was loaded at 1wt%. The oxides of SiO_2 (Q-50; 50 m^2/g, Fuji Silycia), γ-Al_2O_3 (150 m^2/g, W.R.Grace), TiO_2 (JRC-TIO-4; 50 m^2/g, Reference Catalyst supplied by Catalyst Society of Japan), MgO (UBE100A; 100 m^2/g, Ube Industries Ltd.), WO_3, Nb_2O_5 (Reagent Grade, Wako Pure Chemicals Industries, Ltd.) were used as support materials for the catalyst. Zeolite of H-mordenite (SiO_2/Al_2O_3 = 30), H-ZSM-5 (SiO_2/Al_2O_3 = 23-1900) and USY (SiO_2/Al_2O_3 = 29), also used as support material, were supplied by Tosoh Corporation. In this article, H-ZSM-5 (40) will be used to denote H-ZSM-5 with a composition of SiO_2/Al_2O_3 = 40. Laboratory prepared CeO_2-ZrO_2 mixed oxide, NiO and CuO (Reagent grade, Wako pure Chemical, Co., Ltd.) were used as co-catalysts. The mixed oxide CeO_2-ZrO_2 was prepared by co-precipitation from an aqueous solution of cerium nitrate and $ZrO(NO_3)_2$ through hydrolysis with aqueous NH_3, followed by calcination at 773 K in air. The co-catalyst (CeO_2-ZrO_2, NiO or CuO) and Pt/ZSM-5 (40) were mixed in the dry state. Then, the mixture powder was compressed and sieved to obtain catalyst pellets of the desired size.

X-ray Photoelectron Spectroscopy (XPS) measurements were performed (PHI-5500MC; ULVAC-Phai, AlKα ; 1486.6eV ; base pressure = 2 × 10^{-10} Torr) to characterize the oxidation state of the supported Pt. In these experiments, the powder catalysts Pt/SiO_2, Pt/TiO_2, Pt/Nb_2O_5, Pt/WO_3, or Pt/MgO were used.

2. 2 Catalytic reaction tests

A conventional flow system with a tubular fixed bed reactor was used at atmospheric pressure. **Figure 1** shows the experimental setup, which was designed and developed for usage with high molecular weight hydrocarbons (up to n-$C_{16}H_{34}$) .12, 13) The liquid hydrocarbon tank was maintained between 400 - 460 K. Nitrogen flow with a high hydrocarbon content (up to 3%C) could be obtained by bubbling the nitrogen through the hydrocarbon tank. The hydrocarbon concentration was controlled by adjusting the tank temperature and nitrogen flow rate. The entire gas flow line downstream from the hydrocarbon tank was heated at 500 K to avoid deposition of hydrocarbon in the flow system. The gas flow rates of were measured and controlled by mass flow controllers. The concentration of CO, HC, NO, O_2, CO_2, N_2O, NOx, SOx and SO_2 in the inlet/outlet gas was measured by an integrated gas analyzing system (BEX-5000, Best Sokki Co., Ltd.). The catalyst temperature was controlled by an infrared image furnace (ULVAC-RIKO, Inc.).

To determine catalytic activity, two types of reaction tests were employed. One was the conventional steady-state catalytic reaction (steady-state test); the other was carried out while elevating the temperature (light-off test). As the automotive catalyst is typically used under non-steady state conditions, in addition to the steady-state catalytic activity, it is important to determine the catalytic activity under temperature excursion, especially with elevating temperature. Steady-state tests were performed with a simulated exhaust gas containing 150 ppm CO, 1000 ppmC n-$C_{10}H_{22}$, 230 ppm NO, 10% O_2, 6.7% CO_2, 25 ppm SO_2, 5% H_2O and the balancing amount of N_2. The total flow rate was maintained at 10 L/min and 2.0 g of catalyst were used. The catalytic activity was measured in the temperature range 423 K - 773 K. Prior to catalytic activity measurement, the catalyst was pre-treated at 773 K for 15 min in a flowing gas having the composition mentioned above.

The light-off catalytic activity test was performed in the following way: First, the catalyst was pre-treated at 773 K for 15 min with a flowing gas of 10% O_2 in N_2 to remove any hydrocarbon in the catalyst. After pre-treatment, the catalyst was cooled down to 423 K, and then exposed to the simulated exhaust gas (same composition as steady-state reaction). The hydrocarbon concentration (n-$C_{10}H_{22}$) in the outlet gas was monitored until it reached the same level as the inlet gas. Once the catalyst was fully saturated with adsorbed hydrocarbon, the hydrocarbon supply was stopped. The NOx reduction activity was then measured while ramping up the temperature to 773 K at 20 K/min in flowing hydrocarbon-free simulated exhaust gas.

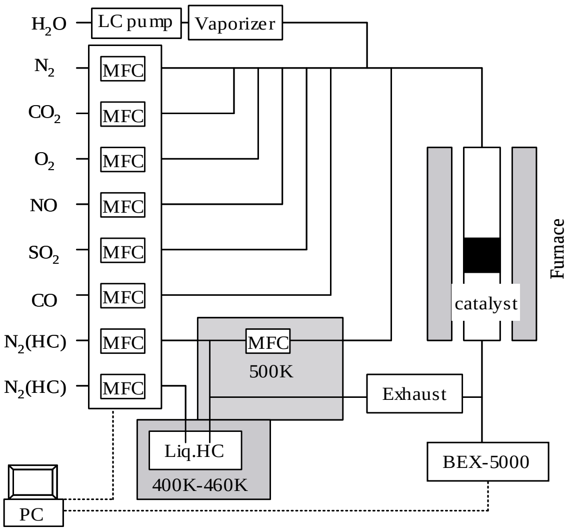

Fig. 1 Experimental setup for catalytic reaction test.

3. Results and Discussions

Figure 2 shows NOx reduction activities of Pt/ZSM-5 (40) measured during a steady-state test, as well as the results of a light-off test that involved raising the temperature at 20 K/min from 423 K to 773 K after hydrocarbon (n-$C_{10}H_{22}$) adsorption at 423 K. In the light-off test, hydrocarbon was not supplied in the reaction gas mixture (in the gas phase), thus the only hydrocarbon available for NOx reduction was hydrocarbon adsorbed on the catalyst. The maximum NOx conversion in the light-off test was higher than that in the steady state reaction. This trend was not observed for Pt/SiO_2, which has no capacity for hydrocarbon adsorption. These results indicate that, if the catalyst is capable of

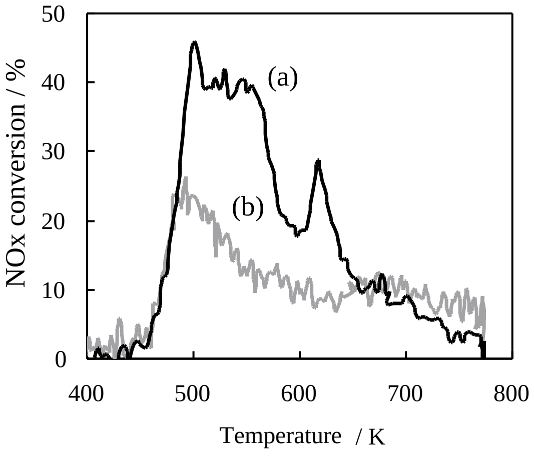

Fig. 2 Catalytic activities of Pt / ZSM-5(40) for NOx reduction by n-$C_{10}H_{22}$. Catalyst : 2.0 g, total flow rate: 10 L/min. (a) Light-off test with adsorbed HC at 393 K. 230 ppm NO, 10% O_2, 150 ppm CO, 6.7% CO_2, 5% H_2O, 25 ppm SO_2 and balanced N_2. (b) NOx reduction by HC in steady state. 230 ppm NO, 10% O_2, 1000 ppmC HC, 150 ppm CO, 6.7% CO_2, 5% H_2O, 25 ppm SO_2 and balanced N_2.

hydrocarbon adsorption, the hydrocarbon desorbing from the catalyst reduces NOx effectively at elevating temperature (i.e., light-off condition). **Figure 3** shows the results of NOx reduction activity for some Pt/zeolite catalysts. NOx conversions were measured over Pt/zeolite catalysts under light-off conditions after hydrocarbon adsorption at 423 K. Hydrocarbon (n-$C_{10}H_{22}$) was supplied until full adsorption. NOx reduction activity was found to depend on the type of zeolite used as support. Pt/USY (29) and Pt/ZSM-5 (40) showed the highest NOx conversion maxima. The temperature at which NOx conversion showed a maximum ranged from 450 K (over Pt/USY) to 610 K (over Pt/mordenite). These temperatures should correlate with the desorption peak temperature of n-$C_{10}H_{22}$ from the catalyst. **Figure 4** shows the effect of composition (i.e., SiO_2/Al_2O_3 ratio) of ZSM-5 on NOx conversions. The maximum NOx conversion was found to depend also on the SiO_2/Al_2O_3 ratio. The maximum of NOx conversion occurred around SiO_2/Al_2O_3 = 40.

One possible reason why NOx reduction activity during the light-off test depends on the type of zeolite could be the differences in their hydrocarbon adsorption capacity. To investigate this possibility, the NOx conversion maxima were plotted against n-$C_{10}H_{22}$ adsorption amount (**Fig. 5**). No correlation was found between the two, indicating that the determining factor is not hydrocarbon adsorption capacity. Hydrocarbon could be activated by the interaction with acidic sites in zeolite while desorbing from it. This process may explain the

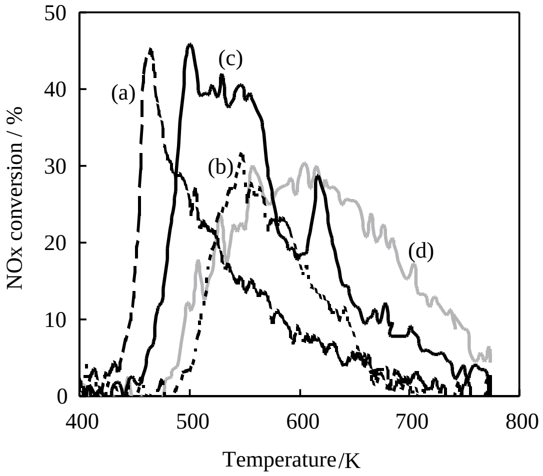

Fig. 3 Catalytic activities of Pt supported catalyst on zeolite for NOx reduction in light-off test. n-$C_{10}H_{22}$ was adsorbed at 393 K until fully adsorption. Catalyst: 2.0 g, total flow rate: 10 L/min., temperature increase rate: 20 K/min., 230 ppm NO, 10% O_2, 150 ppm CO, 6.7% CO_2, 5% H_2O, 25 ppm SO_2 and balanced N_2,
(a) Pt/USY(29), (b) Pt/ZSM-5(23),
(c) ZSM-5(40), (d) Pt/mordenite(30)

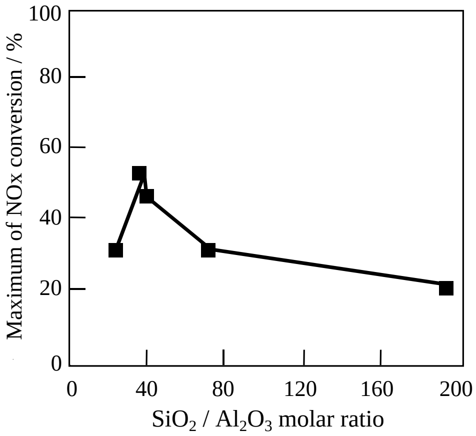

Fig. 4 The dependence of NOx reduction activity on the SiO_2/Al_2O_3 composition of ZSM-5 in light-off test. n-$C_{10}H_{22}$ was adsorbed at 393 K until fully adsorption. Catalyst: 2.0 g of Pt/ZSM-5, total flow rate: 10 L/min., temperature increase rate: 20 K/min., 230 ppm NO, 10% O_2, 150 ppm CO , 6.7% CO_2, 5% H_2O, 25ppm SO_2 and balanced N_2

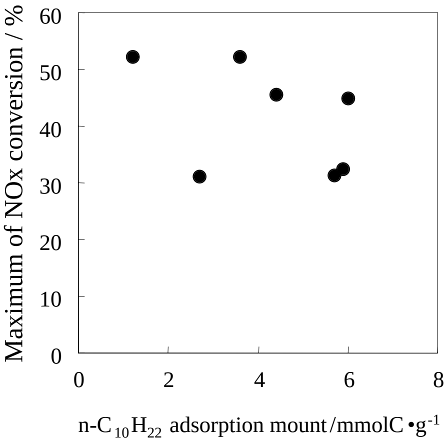

Fig. 5 The correlation between the adsorption amount of HC and NOx reduction activity in light-off test. n-$C_{10}H_{22}$ was adsorbed at 393 K until fully adsorption. Catalyst: 2.0 g, total flow rate: 10 L/min., temperature increase rate: 20 K/min., 230 ppm NO, 10% O_2, 150 ppm CO, 6.7% CO_2, 5% H_2O, 25 ppm SO_2 and balanced N_2

zeolite dependence. Among the different types of zeolites tested, ZSM-5 (40) was found to be most suitable as Pt support for NOx reduction with adsorbed hydrocarbon.

Figure 6 shows the dependence of the NOx conversion maximum on hydrocarbon adsorption amount in the light-off reaction test over Pt/mordenite (30). The amount of adsorbed hydrocarbon was controlled by the duration of hydrocarbon supply to the catalyst at 423 K. The NOx conversion maximum increased with hydrocarbon adsorption until an optimal value of 2.5 mmol C/g, above which it started to decrease. It is known that adsorbed hydrocarbon poisons the catalytic activity of Pt surface,[14, 15)] which is most likely why the NOx conversion maximum decreased above a hydrocarbon adsorption level of 2.5 mmol C/g. To suppress this poisoning, some oxides that have redox activity were added to the catalyst. **Figure 7** shows the NOx reduction activity in the light-off test over catalysts containing CeO_2-ZrO_2, NiO or CuO. The NOx reduction activity of Pt/ZSM-5 (40) without oxide addition is also shown as a reference. The addition of NiO or CeO_2-ZrO_2 improved NOx reduction activity below 473 K, indicating that these oxides promote NOx reduction activity on supported Pt catalyst at low temperatures. This effect is likely caused by active oxygen originating from NiO or CeO_2-ZrO_2, which assists hydrocarbon oxidation at elevating temperature.[16, 17)] By contrast, the addition of CuO caused a decrease in NOx conversion, suggesting that only certain oxides will promote catalytic NOx reduction by adsorbed hydrocarbon.

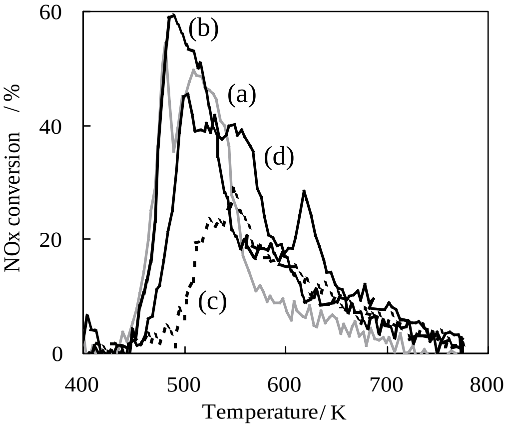

Fig. 7 The promoting effect of the addition of transition metal oxides on NOx reduction activity in light-off test. (a) CeO_2-ZrO_2, (b) NiO, (c) CuO (d) no addition. n-$C_{10}H_{22}$ was adsorbed at 393 K until fully adsorption. Catalyst: 2.0 g of Pt/ZSM-5 (40), total flow rate: 10 L/min., temperature increase rate: 20 K/min., 230 ppm NO, 10% O_2, 150 ppm CO , 6.7% CO_2, 5% H_2O, 25 ppm SO_2 and balanced N_2

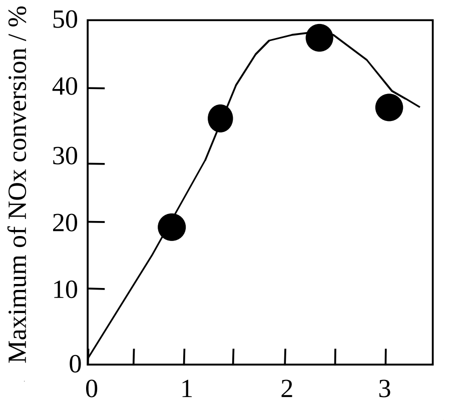

Fig. 6 The promoting effect of HC adsorption on NOx reduction activity in light-off test. n-$C_{10}H_{22}$ was adsorbed at 393K until fully adsorption. Catalyst: 2.0 g of Pt/mordenite (30), total flow rate: 10 L/min., temperature increase rate: 20 K/min., 230 ppm NO, 10% O_2, 150 ppm CO , 6.7% CO_2, 5% H_2O, 25 ppm SO_2 and balanced N_2

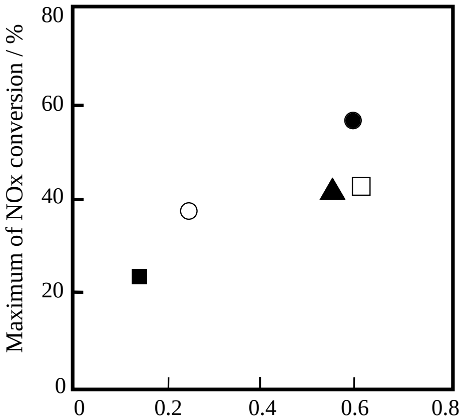

Fig. 8 The correlation between fraction of Pt in metallic state and NOx reduction activity in steady state reaction test. ● ; Pt/SiO_2, ○ ; Pt/ZrO_2, ■ ; Pt/TiO_2, □ ; Pt/Nb_2O_5, ▲ ; Pt/WO_3. Catalyst: 2.0 g, total flow rate: 10 L/min., 230 ppm NO, 10% O_2, 1000 ppmC n-$C_{10}H_{22}$, 150 ppm CO, 6.7% CO_2, 5% H_2O, 25 ppm SO_2 and balanced N_2

Figure 8 shows the correlation between the NOx conversion maximum and the fraction of metallic Pt in various Pt supported catalysts. NOx conversions were measured in steady-state reaction and the fraction of metallic Pt was determined by XPS analysis. The results suggest that metallic Pt is an active site for NOx reduction and that SiO_2 is a suitable support for NOx reduction utilizing hydrocarbons under steady-state conditions. The NOx conversions over Pt/SiO_2, Pt/ZSM-5 (40) and Pt/SiO_2 + ZSM-5 (40) are shown in **Fig. 9**. NOx conversions were measured in light-off test with adsorbed hydrocarbon only. NOx conversion over Pt/SiO_2 + ZSM-5 was similar to that over Pt/ZSM-5 (40). Pt/SiO_2 showed no activity in the light-off test, as it has no hydrocarbon adsorption capacity. These results indicate that, for NOx reduction under light-off conditions, it is not necessary to deposit Pt on zeolite, and that it can be supported on SiO_2 instead. In view of zeolite's poor thermal stability, Pt should be supported on SiO_2 or other thermally stable oxide support, rather than zeolite.[18)]

Based on all these results, we propose a new concept for a NOx catalyst promoted by zeolite and CeO_2-ZrO_2 as shown in **Fig. 10**. Hydrocarbon species adsorbed on zeolite will desorb and migrate to Pt and react with NO as the temperature is raised. Since the adsorbed hydrocarbon was found to poison Pt at low temperature, CeO_2-ZrO_2 was added to supply the active oxygen necessary for suppressing hydrocarbon poisoning. Compared to conventional catalysts, this novel catalyst exhibited superior performance in light-off as well as real automotive exhaust tests.

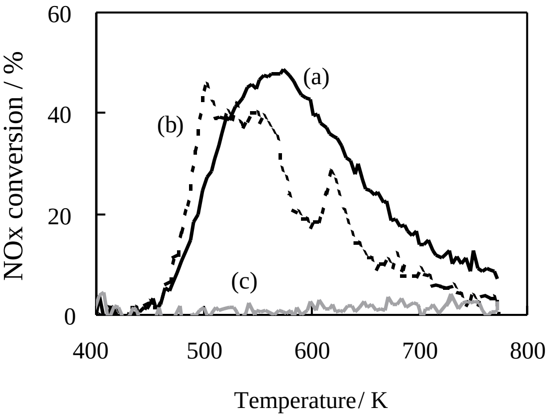

Fig. 9 NOx reduction catalytic activity in light-off test. (a) Pt/SiO_2+ZSM-5(40), (b) Pt/ZSM-5(40), (c) Pt/SiO_2. n-$C_{10}H_{22}$ was adsorbed at 393K until fully adsorption. Catalyst: 2.0 g, total flow rate: 10 L/min., temperature increase rate: 20 K/min., 230 ppm NO, 10% O_2, 150 ppm CO , 6.7% CO_2, 5% H_2O, 25 ppm SO_2 and balanced N_2

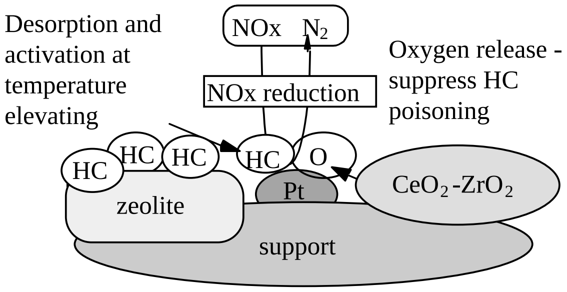

Fig. 10 Conceptual scheme of zeolite and CeO_2-ZrO_2 promoted NOx catalyst.

4. Summary

Adsorbed hydrocarbon on zeolite was found to reduce NOx effectively in oxidizing atmosphere at elevating temperature. Based on this finding, we proposed a catalyst formulation for selective NOx reduction by hydrocarbon with new concept of zeolite and CeO_2-ZrO_2 promotion. This catalyst consists of supported Pt on thermal stable oxides (such as SiO_2), zeolite and CeO_2-ZrO_2. Zeolite and CeO_2-ZrO_2 were added to promote NOx reduction by hydrocarbon on Pt surface. Hydrocarbon adsorbs on zeolite at low temperature and migrates to the Pt surface with increasing temperature to reduce NOx effectively. The active oxygen generated from CeO_2-ZrO_2 suppresses the poisoning effect of hydrocarbon at low temperature, promoting NOx reduction. ZSM-5 (40) and SiO_2 were found to be suitable material as zeolite and oxide support in this catalyst formulation.

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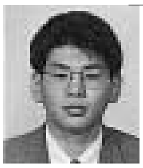
(Report received on July 1, 2002)



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