Selective Catalytic Reduction of NO over PtMo Catalysts with Alkaline or Alkaline Earth Metal under Lean Static Conditions

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The selective reduction of NO on various PtMoX-catalysts (X: Li, Na, K, Mg and Ca) loaded on metal oxides such as SiO_2, Al_2O_3, TiO_2, ZSM-5 and silicallite was studied in an oxygen-rich synthetic mixture simulated exhaust from an automotive lean-burn engine, and compared with that on PtMo/SiO_2, PtNa/SiO_2, and Pt/SiO_2 catalysts. The temperature window for the selective reduction of NO_X on the PtMoLi-, PtMoNa- and PtMoK-catalysts was found to be remarkably wider and to shift to a higher temperature than that on the other catalysts under lean static conditions.

The selective catalytic reduction of NO_X by hydrocarbons and carbon monoxide under excess oxygen conditions has been an object of study for several years. A large amount of research has been carried out to attain a catalyst suitable for practical use. It has been reported that copper ion-exchanged zeolites are efficient for the selective catalytic reduction of NO_X.[1] Some noble metal catalysts are found to be superior in the durability to the copper zeolite system under both the oxidizing and reducing conditions.[1-4] But the noble metal catalysts have a problem because the temperature window for the selective reduction of NO_X, which is from 200°C to 350°C, is too narrow for practical use. Bimetallic PtMo- and PdMo-catalysts have been demonstrated to create new catalytic properties. [5,6] The modification of a noble metal catalyst with Mo provided catalysts with high selectivity for the NO_X to N_2 reaction near the stoichiometric point. The purpose of this study is to examine NO_X reduction on the PtMo-catalysts with various additives and supports under the excess oxygen conditions.

Twelve catalysts composed of Pt, MoO_3, basic additives and various metal oxides were prepared by an impregnation method as summarized in Table 1. The PtMoNa/SiO_2 catalyst was prepared by the same method using SiO_2 powder (AEROSIL TT600, Nippon Aerosil Corp., 200m^2/g), $CH_3COONa{\cdot}3H_2O$ (Wako Pure Chemical Industries), $(NH_4)_6Mo_7O_{27}{\cdot}4H_2O$ (Wako Pure Chemical Industries) and $Pt(NH_3)_2(NO_2)_2$ (Tanaka Precious Metal Co.), and calcined at 500°C for 3h in flowing 10% H_2 / N_2. The Pt, MoO_3 and Na_2O loading amounts were 1.67wt%, 12.3wt% and 0.1wt%, respectively. Other catalysts were prepared in the same way as described above starting from the corresponding additives and supports as shown in Table 1. The prepared catalysts were pressed into disks and pulverized to a 300 ~ 700μm size.

Table 1. Catalyst formulations

Catalyst	Pt loading (wt%)	MoO_3 loading (wt%)	additive	loading (wt%)	Support
PtMoNa/SiO_2	1.67	12.3	Na_2O	0.1	SiO_2
PtMoLi/SiO_2	1.67	12.3	Li_2O	0.1	SiO_2
PtMoK/SiO_2	1.67	12.3	K_2O	0.1	SiO_2
PtMoMg/SiO_2	1.67	12.3	MgO	0.1	SiO_2
PtMoCa/SiO_2	1.67	12.3	CaO	0.1	SiO_2
PtMoNa/Al_2O_3	1.67	12.3	Na_2O	0.1	Al_2O_3
PtMoNa/TiO_2	1.67	12.3	Na_2O	0.1	TiO_2
PtMoNa/ZSM-5	1.67	12.3	Na_2O	0.1	ZSM-5
PtMoNa/silicallite	1.67	12.3	Na_2O	0.1	silicallite
PtMo/SiO_2	1.67	12.3	-	0	SiO_2
PtNa/SiO_2	1.67	0	Na_2O	0.1	SiO_2
Pt/SiO_2	1.67	0	-	0	SiO_2

The laboratory reactor system used in this experiment was similar to a previously described system.[7] The feed compositions and reaction conditions used in this study were as follows: The simulated oxygen-rich synthetic mixture consisted of 4.3% O_2, 0.12% NO, 800ppm C_3H_6, 0.12% CO, 400ppm H_2, 12.3% CO_2, 3% H_2O, and the balance N_2. This mixture simulated an air to fuel (A/F) ratio of 18 (lean mixture). For each light-off test, catalysts were exposed to the simulated exhaust at 3.3l/min while the temperature was decreased from 600°C to 100°C at 5°C/min and at 9.91×10^{-3}g·sec/cc W/F. The activity was determined by continuously measuring the concentration of NO_X ($NO+NO_2$) with a chemiluminescent NO_X analyzer (Horiba, MEXA-8120).

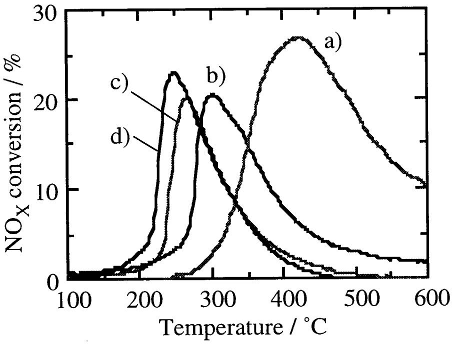

Figure 1. NO_X conversion efficiency as a function of temperature in simulated oxygen-rich feedstream. The following catalysts are indicated: a) PtMoNa/SiO_2, b) PtMo/SiO_2, c) PtNa/SiO_2 and d) Pt/SiO_2. Calcination conditions : 500°C, 10% H_2/N_2, 3h. The reactions were carried out on a 0.5g of sample exposed to the simulated exhaust gas composed of 4.3% O_2, 0.12% NO, 800 ppm C_3H_6, 0.12% CO, 400ppm H_2, 12.3% CO_2, 3% H_2O, and the balance N_2 at 3.3l/min.

Figure 1 shows the conversions of NO_X on the PtMoNa/SiO_2, PtMo/SiO_2, PtNa/SiO_2 and Pt/SiO_2 catalysts as a function of temperature. The Pt/SiO_2 and PtNa/SiO_2 catalysts had the maximum conversions of NO_X at temperatures from 250 to 260°C. The conversions of NO_X by these catalysts rapidly decreased with increasing temperature above 260°C. These temperature dependences of the NO_X selective reduction were the same as that of previously reported Pt catalysts.[2,3] The temperature of the maximum NO_X conversion (300°C) on the

$PtMo/SiO_2$ catalyst was about 50°C higher than that on the Pt/SiO_2 catalyst. The conversion of NO_X gradually decreased with increasing temperature above 300°C. On the other hand, the maximum NO_X conversion temperature (400 ~ 450°C) on the $PtMoNa/SiO_2$ catalyst was about 150 to 250°C higher than that on the Pt/SiO_2 catalyst. These results show that the addition of both Na_2O and MoO_3 plays a significant role in the reactivity of Pt on the $PtMoNa/SiO_2$ catalyst.

Figure 2 shows the conversions of NO_X on the $PtMoLi/SiO_2$, $PtMoK/SiO_2$, $PtMoMg/SiO_2$ and $PtMoCa/SiO_2$ catalysts as a function of temperature. The $PtMoLi/SiO_2$ and $PtMoK/SiO_2$ catalysts had the maximum conversion of NO_X at temperatures from 400 to 500°C. The temperature dependence of NOx conversion of these catalysts had the features similar to the $PtMoNa/SiO_2$ catalyst in Figure 1. On the other hand, the $PtMoMg/SiO_2$ and $PtMoCa/SiO_2$ catalysts had the maximum conversion of NO_X below 350°C, and the features were similar to the $PtMo/SiO_2$ catalyst in Figure 1. These results show that the addition of alkaline metals to the $PtMo/SiO_2$ catalyst had a significant effect on the shift in the temperature windows of the NO_X conversion on the PtMo catalysts.

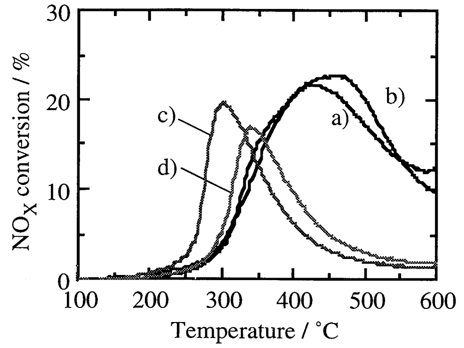

Figure 2. NO_X conversion efficiency as a function of temperature in simulated oxygen-rich feedstream.
a) $PtMoLi/SiO_2$, b) $PtMoK/SiO_2$, c) $PtMoMg/SiO_2$ and d) $PtMoCa/SiO_2$. Calcination and the reaction conditions are shown in Figure 1.

Figure 3 shows the conversions of NO_X on $PtMoNa/Al_2O_3$, $PtMoNa/TiO_2$, PtMoNa/ZSM-5 and PtMoNa/silicallite catalysts as a function of temperature. The $PtMoNa/Al_2O_3$ and $PtMoNa/TiO_2$ catalysts had the maximum conversions of NO_X below 300°C, and had features similar to the $PtMo/SiO_2$ catalyst. The conversions of NO_X on PtMoNa/ZSM-5 and PtMoNa/silicallite catalysts were higher than those of the $PtMoNa/Al_2O_3$ and $PtMoNa/TiO_2$ catalysts at temperatures from 400 to 500°C. But the NO_X conversion curves of these catalysts were not similar to that of the $PtMoNa/SiO_2$ catalyst. These results show that the support also affects the reaction characteristics of the PtMoNa catalysts.

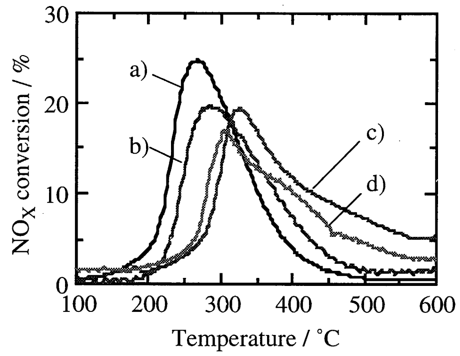

Figure 3. NO_X conversion efficiency as a function of temperature in simulated oxygen-rich feedstream.
a) $PtMoNa/Al_2O_3$, b) $PtMoNa/TiO_2$, c) PtMoNa/ZSM-5 and d) PtMoNa/silicallite. Calcination and the reaction conditions are shown in Figure 1.

A number of papers have already described that the temperature of the maximum NO_X conversion for the selective reduction of NO_X on Pt catalysts shifted as the Pt loadings,[3] Pt precursor,[3] and aging conditions changed. In these cases, the maximum NO_X conversion decreased with increasing temperature. On the other hand, for the selective reduction of NO_X on the $PtMo/SiO_2$ catalysts with alkaline metal additives, the maximum NO_X conversion increased as its temperature increased. Also, these catalysts had a upper temperature window of 350°C for the selective NO_X reduction. These results are assumed to be due to the decrease in the affinity between oxygen and Pt by the addition of Mo and alkaline metals on the SiO_2 support.

References and Notes

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