Mechanistic study of NO_x storage and reduction behavior over Pt /alkali metal nitrate nanocomposite catalysts supported on TiO_2

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Introduction

Since the pioneering work of NO_x storage-reduction (NSR) catalysts by Toyota's research group, many studies have been reported on the mechanism of NSR reaction over Pt-BaO/Al_2O_3 catalysts. The generally accepted mechanism on this reaction is "NO_2 transfer from Pt to BaO" forming $Ba(NO_3)_2$ surface layers. Recently, we have found that K-titanate-nanobelt (KTN: $K_2Ti_8O_{17}$) supported Pt/KNO_3 NSR catalyst exhibited high NO_x storage capacity and excellent redox behavior, and proposed a novel "K^+ transfer mechanism" from and back to K rich titanate surface layers[1].

In the present study, we have employed different crystalline structure TiO_2 's (P-25, ST-01, MT-150A) with various loading amounts of Pt (0.5-5 wt%) and KNO_3(10-41 wt%) to study the activity and selectivity controlling factors for NSR process.

Materials and Methods

The K-titanate nanobelt ($K_2Ti_8O_{17}$: KTN) was prepared by hydrothermal treatment, using TiO_2 (P-25) and KOH. Various amounts (x = 0, 20, 26, 33, 41 wt%) of KNO_3 and 1.5 wt% Pt were supported on KTN, ST-01(Anatase;270m^2)), MT150A(Rutile;100m^2) and P-25(A/R=0.8, 50m^2) supports by a conventional impregnation method. After reduction of a catalyst (0.2g) at 350°C, a NO_x storage process (lean; 80mL/min of 930ppm NO/7%O_2/He) was performed on a gas flow system and the output gas was analyzed by mass spectroscopy, followed by a rich process of 80mL/min of 4%H_2/He flow. The lean-rich cycle experiments were carried out using an interval of 6 min of NO_x (930ppm) and 4 min of H_2 (4%) with 80ml/min flow (catalyst; 0.1g).

Results and Discussion

Fig.1 shows the dependence of the NO_x storage capacity upon the added amount of KNO_3 on various supported catalysts. In the case of KTN and ST-01 catalysts, the highest storage capacity of 2.3-2.4 mmol/g was achieved when 33 wt%KNO_3 was loaded. In the case of KTN catalyst, TEM images showed that the nanobelt structure was completely maintained even after the redox cycle, when the amount of modified KNO_3 was lower than 26 wt %. P-25 and MT-150A supported catalysts exhibited similar dependency although the maximum stored amounts were less than former ones. From these results we can conclude that NO_x storage capacity is mainly determined by the loaded amount of KNO_3 with no direct relation to the crystalline structure of the support.

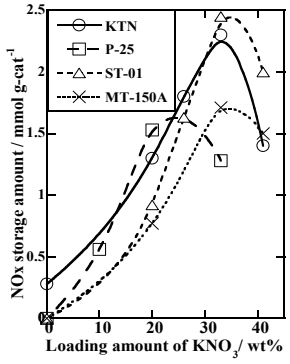

Fig. 1. KNO_3 loading dependency

Table 1. Full trapping period & amounts of stored NO and desorbed N_2 over various catalysts

Catalysts[1)] (TiO_2 crystallinity)	Surf. area (m^2/g)	Pt size determ. by CO ads. (& TEM)	Full trapping period[2)] (min)	NO stored[2)] (mmol/g)	N_2 desorb.[3)] (mmol/g)
ST-01(Anatase)	71.6	2.9nm (2.5nm)	18	2.25	1.11
MT150A(Rutile)	15.4	4.1nm (5.2nm)	1	1.75	0.66
P-25(A/R=0.7)	14.9	3.7nm (3.5nm)	8	1.28	0.57
KTN	108	2.1nm (1.5nm)	25	2.36	1.15

1) 1.5wt%Pt-33wt%KNO_3 0.1g , 2)Lean:80mL/min-930ppmNO/7%O_2/He, 3)Rich:80mL/min-4%H_2/He

Table 1 summarizes NOx storage and reduction properties of 1.5wt%Pt-33wt% KNO_3 catalysts supported on various supports. The results indicated that full NO trapping periods and NO stored amounts were strongly dependent on Pt particle sizes, which seemed to be determined by the surface area of TiO_2 supports (and/or their crystallinity). The KTN and ST-01 (anatase) supported ones showed more efficient catalytic behavior than others, which showed longer full trapping periods; 25 min and 18 min respectively. Fig.2 shows the lean-rich cycle experiments over 1.5wt%Pt-33KNO_3/KTN and 1.5wt%Pt-33KNO_3/ST-01 catalysts. In the former case, almost all of the NO_x was stored for 6 min and the capacity was completely recovered by a 4 min H_2 reduction, indicating an excellent NO_x trapping capacity with high stability. However, in the latter case, a considerable amount of NO was detected at the later stage of the lean cycle, indicating an important role of the ordered-layer structure of K cations although its full NO trapping period (18 min) was not so different from KTN's 25min. Moreover, in the cases of KTN supported catalysts, XRD, XPS and FT-IR measurements exhibited the formation of well dispersed KNO_3 species during the NO_x storage process and the formation of unique K-rich surface layers over the bulk during the reduction process. From these experimental results, we could conclude the following three factors were important as the NSR catalyst in the Pt-K/TiO_2.

(1) smaller Pt metal particles for rapid NO oxidation and KNO_3 reduction,

(2) facile migration of K cations from and back to the K-rich layers during NOx storage and reduction process,

(3) existence of a certain surface structure to maintain high dispersion of K^+ cations.

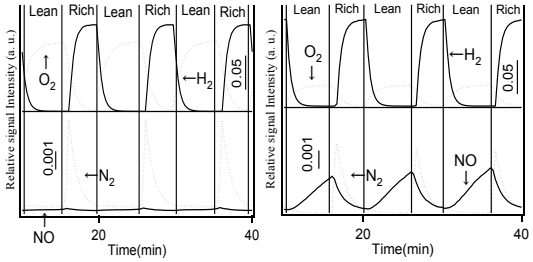

Fig. 2 NOx storage- reduction cycles at 350℃ over (a) KTN and (b) ST-01 supported catalysts

Significance

Excellent NO_x storage properties were realized by adding KNO_3 to Pt/KTN catalysts. Maintaining the nanobelt structure and optimizing the amount of KNO_3 were the key factors to obtain high NO_x storage capacity. The segregation of K^+ from and back to the lattice of nanobelt wall may be the NO_x storage and reduction mechanism of these materials.

References

[1] W. Shen, A. Nitta, Z. Chen, T. Eda, A. Yoshida, S. Naito, J. Catal., (2011) *280*, 161-167.