Pt-B Catalyst Supported on Phosphates for Controlling Emissions of NOx, CO and Hydrocarbon at Low Temperatures

Masaharu Hatano * and Hiroo Kinoshita
Next Generation Catalyst Research Institute, Co., Ltd., Kanagawa Science Park, Takatsu-ku, Kawasaki 213

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The performances of B-containing Pt catalysts supported on phosphates as an emission control catalyst were investigated for the reaction in an oxidizing atmosphere. Among them, rare earth phosphate supports showed not only the highest NO reduction activity, but also the highest CO and C_3H_6 oxidation activity at lower temperatures.

Noble metal catalysts supported on alumina with several additives are successful emission control catalysts, which have been extensively used and contributed to preserving the global environment today. However, there is a strong need to improve their activity at lower temperatures.[1-3] This paper describes the catalytic activities of platinum catalyst supported on various phosphates with a boron oxide additive as an active emission control catalysts at lower temperatures.

Phosphate supports were prepared by coprecipitation from the mixed aqueous solution of metal nitrate and phosphoric acid (metal atom/phosphoric acid = 1 molar ratio). A 10% ammonia aqueous solution was added to the above solution until the pH of the solution reached 7.0. The obtained precipitate was dried for 40 h at 383 K and calcined in air for 3 h at 673 K.

Pt-Boron/phosphate catalysts were prepared by impregnation with boric acid and tetraammine platinum nitrate followed by calcination in air at 873 K for 5 h. The platinum and boron loadings were 2 and 5 wt%, respectively. The catalysts were pelletized, and sieved to 0.5-1.0 mm particles.

The catalytic tests were carried out using a fixed-bed flow reactor with simulated lean-burn exhaust gas. The gas mixture consisting of 1000 ppm NO, 1000 ppm C_3H_6, 6% O_2, 1200 ppm CO, 10% CO_2, 400 ppm H_2 and 10% H_2O in N_2 was fed into 0.45 g catalyst bed at the rate of 2.5 l/min. Gas hourly space velocity at this condition was between 400000-500000 h^{-1}. The activities of the catalysts were measured between 473 and 873 K. The measurement was done after a steady-state was obtained at each temperature. The gas composition was monitored by the analyzer equipped with chemiluminescence detector for NOx, FID detector for total hydrocarbon and IR detector for CO.

Figures 1 and 2 show the effect of reaction temperatures on the conversions of NOx, CO and C_3H_6 over Pt-B/yttrium phosphate. For comparison, the activity of Pt/alumina catalyst was also plotted. Although the conversions of CO and C_3H_6 exceeded 98% at higher temperatures (>600 K), maximum NO conversion was observed for both catalysts. Pt-B/yttrium phosphate showed higher NO maximum conversion than Pt/Al_2O_3. In addition, it is obvious from the temperature dependency profiles that Pt-B/yttrium phosphate has a great advantage over Pt/Al_2O_3 in conversions of NOx, CO and C_3H_6 at lower temperatures (<550 K).

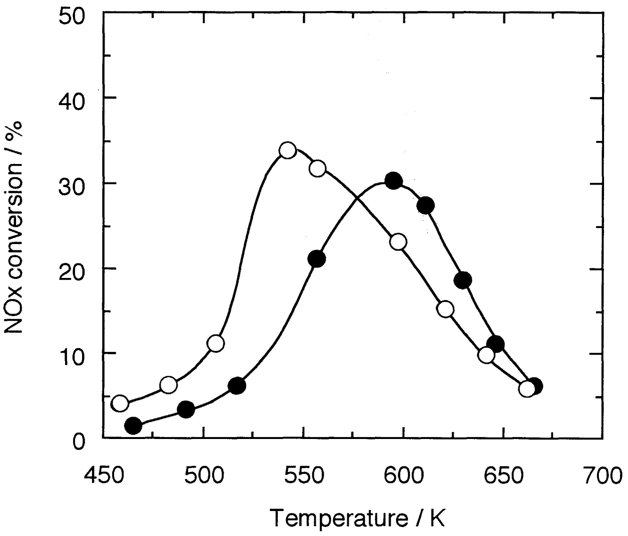

Figure 1. Temperature dependency of NOx conversion over Pt-B/YPOx (○) and Pt/Al_2O_3 (●).

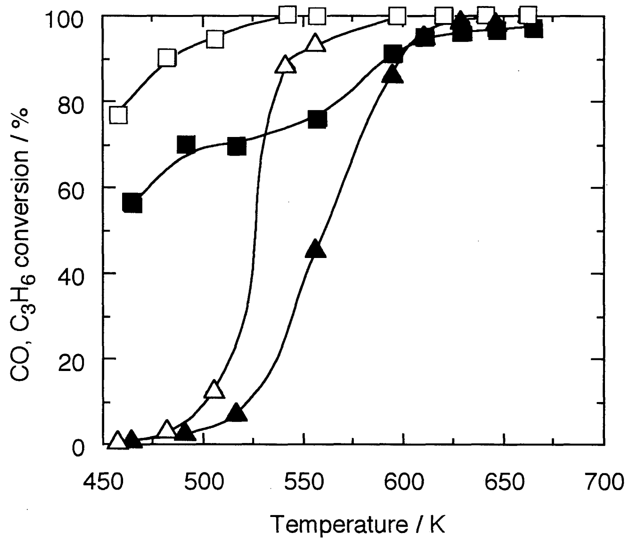

Figure 2. Temperature dependency of CO and C_3H_6 conversions over Pt-B/YPOx (CO:□, C_3H_6:△) and Pt/Al_2O_3 (CO:■, C_3H_6:▲).

Catalytic activities were measured for a series of Pt-B /phosphate catalysts. Figure 3 summarizes the conversions of NOx, CO and C_3H_6 at 523 K. Among the supports tested, rare earth (Y, La, Ce) phosphates (REPO) were the most active support at 523 K. Conversions of NOx and C_3H_6 over rare earth phosphates were remarkably high in comparison with alumina support. As to the effect of boron, the catalytic activity of

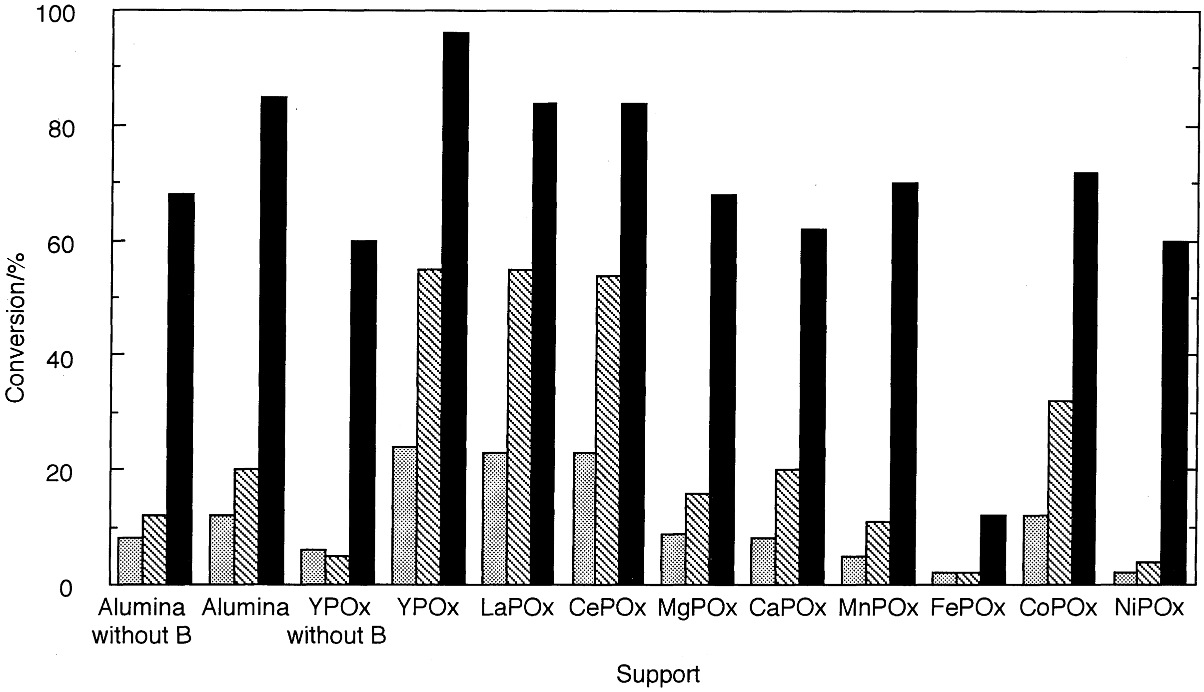

Figure 3. Effect of support on NOx (▒), C_3H_6 (▨), and CO (■) conversions at 523 K.

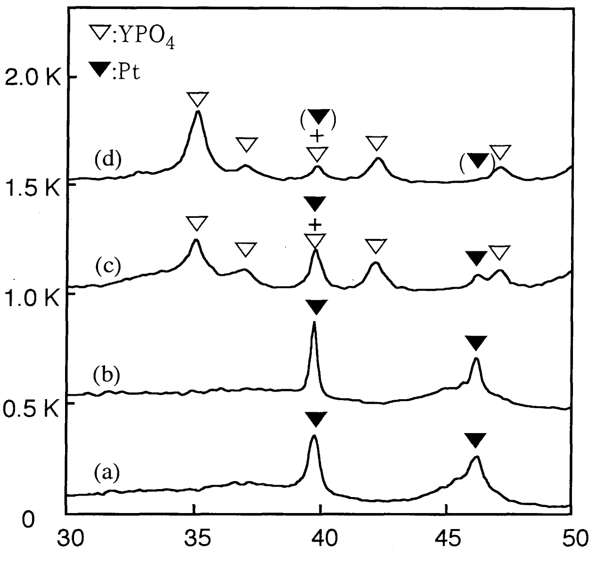

Figure 4. XRD results of (a)Pt/Al_2O_3, (b)Pt-B/Al_2O_3, (c)Pt/YPO_4, (d)Pt-B/YPO_4.

Pt/REPO at 523 K was drastically enhanced by B addition. In the case of yttrium phosphate, NOx, C_3H_6 and CO conversions increased by B-addition from 6, 5 and 60% to 24, 55 and 96%, respectively, while their increases were smaller in the case of alumina support as shown in Figure 3. This result indicates that the combination of boron and REPO is more favorable for low temperature activity than that of boron and alumina, while enhancement of the reactivity by B-addition was observed in both cases. Alkaline earth and first row transition metal phosphates were less active, although they showed higher activities at higher temperatures. However, Pt-B catalyst supported on oxide supports such as Fe_2O_3, Co_3O_4, NiO showed no activity at this conditions. It appears that the phosphate supports are potential materials for the emission control catalyst, but its activity remains to be improved.

Pt-B/yttrium phosphate was characterized by XRD as shown in Figure 4. Its diffraction patterns showed peaks due only to yttrium phosphate (YPO_4), but no boron compound and Pt peaks were observed. Pt/YPO_4, Pt/Al_2O_3 and Pt-B/Al_2O_3, on the contrary, clearly exhibited the existence of cubic Pt metal phase. The high activity at low temperatures on Pt-B/REPO may be explained as due to highly dispersed Pt on the REPO surface.

In conclusion, Pt-B/phosphate catalysts, especially Pt-B/REPO showed high activity for the simultaneous removal of NOx, CO and C_3H_6 at low temperatures. It was found that the associative effect of boron with REPO support caused active Pt state for low temperature reaction.

References

1 A.S. Sass, V.A. Shvets, G.A. Savel'eva, N.M. Popova, and V.B. Kazanskii, *Kinet. Katal*, **27**, 894 (1986).

2 S.E. Golunski, H.A. Hatcher, R.R. Rajaram, and T.J. Truex, *Appl. Catal. B*, **5**, 367 (1995).

3 R.S. Drago, K. Jurczyk, D.J. Singh, and V. Young, *Appl. Catal. B*, **6**, 155 (1995).