

# A novel boron nitride supported Pt catalyst for VOC incineration

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## Abstract

Low-crystalline hexagonal boron nitride (h-BN) and  $\gamma$ -alumina supported Pt catalysts were employed to investigate the catalytic destruction of volatile organic compounds (VOC). The 0.3 wt.% Pt catalysts were prepared via incipient wetness method using  $\text{H}_2\text{PtCl}_6$  as precursor. The oxidation of volatile gasoline was performed in a concentration of 2500 ppmv with volume hour space velocity (VHSV) near  $20\,000\text{ h}^{-1}$  from 100 to  $500^\circ\text{C}$ . Instead of deactivation, the activity of Pt/h-BN increased significantly in the second run of the oxidation reaction. The light-off temperature (50% conversion) decreased from 210 to  $160\text{--}170^\circ\text{C}$  in the second run of oxidation. Furthermore, 95% conversion was achieved at less than  $200^\circ\text{C}$ . Meanwhile, the Pt/ $\gamma\text{-Al}_2\text{O}_3$  became deactivated in the second run of oxidation. The activity of Pt/h-BN was maintained for three temperature cycles. Long-term oxidation proved that Pt/h-BN activity did not decline over up to 80 h. The positive binding energy shift from XPS revealed that a few boron oxide impurities contaminated on the h-BN surface, these provided the anchorage for the Pt clusters. Metallic Pt surface was oxidized to PtO during the initial oxidation, thus enhancing the oxidation activity. Based on irreversible  $\text{H}_2$  chemisorption, the platinum dispersion of Pt/h-BN were near 20% and did not change after oxidation at  $500^\circ\text{C}$ . Metal sintering was minimal, owing to the high thermal conductivity of h-BN, which prevented any hot spots of oxidation on Pt sites. In sum, experimental results demonstrated that Pt/h-BN was a promising catalyst for VOC destruction. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Catalytic deep oxidation; Pt; Hexagonal BN;  $\gamma$ -Alumina; VOC; Gasoline

## 1. Introduction

Volatile organic compounds (VOC) are a primary air pollutant. A high temperature must be maintained for complete combustion of VOC to occur, and this can be costly as supplemental fuel is often required. In compliance with the stringent environmental regulations, catalytic oxidation can effectively destroy VOC. The advantage of low oxidation temperature is to reduce fuel consumption particularly for large volumes of

dilute VOC polluted air. Supported Pt alumina or other metal oxides are conventional catalysts for such applications and have received broad attention [1].

Traditional metal oxide supports, such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and zeolite possess rather low thermal conductivity and transform with water vapor at high temperature. The sintering of supported-metal may be severe on hot spots during the deep oxidation of VOC in highly exothermic reactions. The support characteristic also plays an important function in supported noble metal catalysts. Some metal-support interaction generally exists in most oxide-supported metal catalysts and brings about a negative influence on the catalytic activity [2]. Chloride is another negative impact on

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catalytic activity of noble metals by forming oxy-chloride. The species of  $\text{PtO}_x\text{Cl}_y$  would suppress the oxidation activity substantially [3]. Generally, a noble metal is often dissolved in hydrogen chloride when it is employed as a precursor solution during catalyst preparation. Unfortunately, the elimination of chloride from traditional oxides is tedious. Therefore, one way to avoid these disadvantages would be the use of a non-oxide material as the support.

Our previous results reported that activated carbon supported Pt catalysts exhibited several advantages over the traditional Pt/ $\gamma$ -alumina in VOC oxidation, such as hydrophobic surface, chlorine resistance and negligible metal–support interaction. The complete destruction of VOC was achieved at lower temperatures with activated carbon support than those with  $\gamma$ -alumina [4]. However, carbon support tends to be burned off if oxidation is carried out at high temperature (greater than 250°C). In a continued search for non-oxide supports, we demonstrate a new non-oxide, hexagonal boron nitride (h-BN), as a support. The h-BN keeps the advantages of activated carbon without the weakness of being oxidized at high temperature. The h-BN has both crystalline and electronic structure similar to those of graphite, and possesses excellent chemical stability as well as high thermal conductivity. The h-BN is not attacked by water and any mineral acids except hydrogen fluoride, and in general, has been found to be very resistant to other kinds of chemical attack [5]. A particular advantage of h-BN is its extremely high thermal stability against volatilization up to 800°C in air [6]. The total oxidation of VOC employing h-BN supported Pt catalysts is investigated herein.

## 2. Experimental

### 2.1. Catalysts preparation and characterization

The h-BN powder was specially prepared and supplied by the High Performance Material Inc., Taiwan, ROC. The h-BN was calcined at a temperature of 800°C, lower than the typical temperature of over 1000°C during synthesis. X-ray diffraction (XRD) spectra revealed that its crystallinity was low compared with that of typical h-BN. Another support,  $\gamma$ -alumina (Merck, USA) was chosen for comparison.

Platinum catalysts were prepared by an incipient wetness technique aiming for 0.3 wt.% Pt with h-BN and  $\gamma$ -alumina as supports designated as Pt/h-BN and Pt/ $\gamma$ - $\text{Al}_2\text{O}_3$ , respectively. Precursor salt,  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$  purchased from Aldrich (USA), contained ~40 wt.% of platinum. For better soaking on the hydrophobic h-BN support, methanol was chosen as the diluting solvent. The quantity of methanol required to completely fill the pore volume of support was predetermined. The amount of methanol-soluble Pt solution applied for the impregnation was typically from 95 to 100% of the absorptive capacity of support. The Pt concentration in solution was controlled to allow the total absorption by the support to achieve the desired 0.3 wt.% level of Pt in the catalyst. After impregnation, the catalysts were dried at ambient temperature overnight. All the catalysts were then reduced at 300°C for 1 h, with a 3°C/min rise from room temperature under a flow of 20%  $\text{H}_2$  in  $\text{N}_2$  mixture, then stored in a desiccator for later use. The precise Pt loading of the catalysts was measured using the wet chemical method. Pt/h-BN was weighed, then rinsed and stirred in aqua regia. The leached solution was filtered and diluted with deionized water to the appropriate concentration. Pt/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalyst was dissolved in HF and aqua regia, then diluted with deionized water to the appropriate concentration. A series of standard Pt solutions (diluted from Aldrich platinum AA solution) were employed to establish calibration curves. The Pt concentration of solution was measured by UV adsorption at 261.8 nm [7], the percentage weight of Pt loading was then calculated. The Pt dispersion was estimated from the irreversible  $\text{H}_2$  chemisorption [8].

Temperature programmed reduction (TPR) was performed on both Pt catalysts. Fresh catalyst (0.2 g) was first oxidized under an air flow at 300°C for 2 h, cooled to near 50°C, purged with Ar, then switched to a 5%  $\text{H}_2$ /Ar flow and the temperature was increased to 650°C with a heating rate of 10°C/min. The specific surface area of catalyst was calculated from the  $\text{N}_2$  adsorption at 77 K. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were employed to examine the morphology of the catalysts. The crystallinity was analyzed by XRD. X-ray photoelectron spectroscopy (XPS) was conducted on a MicroTech MT500 instrument. The spectrometer vacuum was in the  $10^{-9}$  Torr range. The hemispherical analyzer was operated in the fixed retarded ratio near

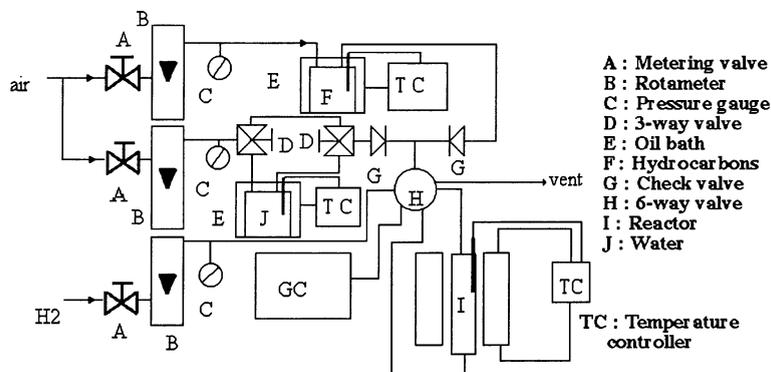


Fig. 1. Schematic of reactor system.

11. Mg K $\alpha$  radiation ( $h\nu = 1253.6$  eV) was used as X-ray source. Catalyst (in powder form) was affixed onto the sample holder by silver glue. Silver (3d $_{5/2}$ , 368.3 eV) and carbon (1s, 284.5 eV) were used as an internal standard for binding energy calibration.

## 2.2. Catalytic oxidation

The unleaded octane 95 gasoline was purchased from a gas station of China Petroleum Corporation (CPC), Taiwan, ROC. This gasoline has a specification of about 35 vol.% of aromatics. Reagent-grade *iso*-hexane purchased from Alps Chemical Co. (Taiwan, ROC) was used to represent one of the major components of gasoline vapor. Fig. 1 depicts the schematic of reactor system. An air stream, which bubbled through a saturator filled with liquid hydrocarbon carried the volatile vapor. The concentrations was regulated by the temperature of the saturator and was mixed with an additional air stream. The concentrations of gasoline vapor and *iso*-hexane were 2500 and 600 ppmv, respectively, and they were always confirmed by gas chromatography (GC) before the reaction. The reactions were performed at temperatures ranging from 90 to 500°C under atmospheric pressure. The catalyst (0.3 g) was charged in the middle of a straight-tube Pyrex reactor with a 16 mm i.d. A thermocouple was placed in the center of the catalyst bed to record reaction temperature and also to control the furnace temperature. In several experiments, the catalyst was pretreated to 300°C for 2 h then cooled to room temperature in air or nitrogen before switching to reactant stream. The reactant flows were tuned to

a volume hour space velocity (VHSV) of 20 000 h $^{-1}$ . Since  $\gamma$ -alumina is denser than h-BN, the reactant flow rate was reduced accordingly for the same VHSV to be maintained within Pt/ $\gamma$ -Al $_2$ O $_3$ . The reaction temperature usually was increased from low to high, and was decreased again to low temperature in some cases to check consistency. Typically, an accumulated run time lasted nearly 30 h per catalyst. An on-line HP6890 GC equipped with thermal conductivity detector (TCD) and flame ionization detector (FID) in series measured both reactants and products. Separation of H $_2$ O, CO $_2$  and most light hydrocarbons was accomplished with an HP-PLOT Q 30 m capillary column. The primary oxidation products were found to be CO $_2$  and H $_2$ O only. That is, under experimental conditions carbon monoxide and other partial oxidation products were virtually undetectable. Thus, the conversion was calculated based on the total hydrocarbon remaining after oxidation. The carbon balance between reactants and products were assessed and the maximum difference was within 10%. The conversion was calculated based upon the total carbon as gasoline volatile is a mixture. A blank test was conducted using h-BN without Pt loading. No activity was observed up to 250°C.

## 3. Results and discussion

### 3.1. Characteristics of catalysts

Table 1 lists the specific surface areas of supports both before and after VOC oxidation. The initial surface area of h-BN and  $\gamma$ -Al $_2$ O $_3$  are 70 and 99 m $^2$ /g,

Table 1  
Properties of Pt catalyst

Catalysts	Fresh (m <sup>2</sup> /g)	VOC oxidation <sup>a</sup> (m <sup>2</sup> /g)	Average particle size <sup>b</sup> (μm)
Pt/h-BN	70	69	10
Pt/γ-Al <sub>2</sub> O <sub>3</sub>	99	84	180

<sup>a</sup> VOC oxidation: 2500 ppmv gasoline vapor in air up to 500°C.

<sup>b</sup> Average particle size measured by laser scattering (Coulter LS230).

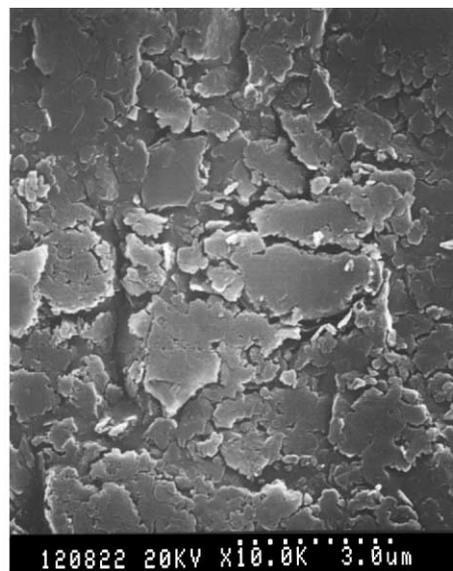
respectively. Generally the surface area of crystalline h-BN is very low (e.g. 1–2 m<sup>2</sup>/g). The high surface area of our h-BN was due to the low processing temperature according to supplier, which in turn prevented it from transforming to high crystallinity during synthesis. Fig. 2a and b display the SEM and TEM micrographs of h-BN and Pt/h-BN, respectively. The h-BN particles appear flaky and have an irregular shape. A few Pt clusters, 5–15 nm in size, were observed in TEM micrograph.

The potential loss of Pt on Pt/h-BN during reaction may be attributed to weak binding between metal and h-BN which has low surface energy. Table 2 lists the accurate Pt loading measured from wet chemical analysis as well as the dispersion from irreversible H<sub>2</sub> chemisorption. The Pt loadings nearly achieved the intended value, i.e. 0.3 wt.%, in preparation using incipient wetness technique. For fresh hydrogen reduced catalysts, the dispersion of Pt/h-BN and Pt/γ-Al<sub>2</sub>O<sub>3</sub> were 19 and 30%, respectively. The variation of Pt dispersion could be due to the diverse specific surface areas among supports (Table 1). The Pt loading and dispersion remained unchanged after oxidation. Fig. 3 shows the XPS of two h-BNs. When compared with that of a standard highly crystalline hexagonal BN, the binding energy of h-BN indicates a positive 0.7 eV shift. Being calcined at lower temperature, our h-BN may have residual B–O bonds which induce a positive binding energy shift. The residual B–O bond provides

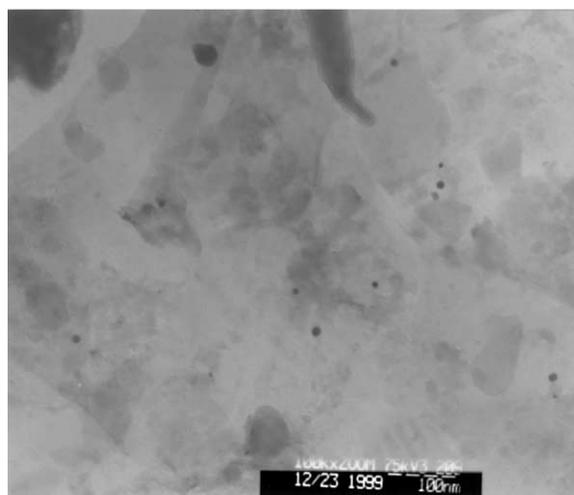
Table 2  
Platinum loading and dispersion of catalysts

Catalysts	Fresh (wt.%)	Dispersion (%)	VOC oxidation <sup>a</sup> (wt.%)	Dispersion (%)
Pt/h-BN	0.30	19	0.29	19
Pt/γ-Al <sub>2</sub> O <sub>3</sub>	0.29	30	0.28	29

<sup>a</sup> VOC oxidation: 2500 ppmv gasoline vapor in air up to 500°C.



(a)



(b)

Fig. 2. (a) SEM of h-BN; (b) TEM of Pt/h-BN.

an excellent anchor for Pt cluster, thus preventing Pt loss during catalytic oxidation.

### 3.2. VOC deep oxidation

Generally, depending upon its source, the volatile compounds from gasoline consist of a C<sub>4</sub>–C<sub>7</sub> mixture, which includes paraffins, olefins and aromatics.

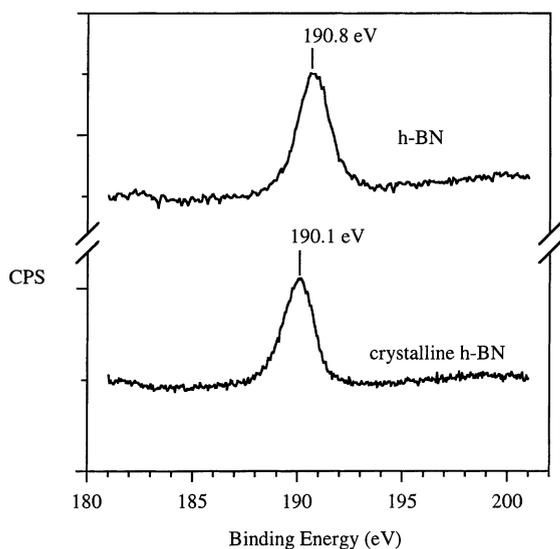
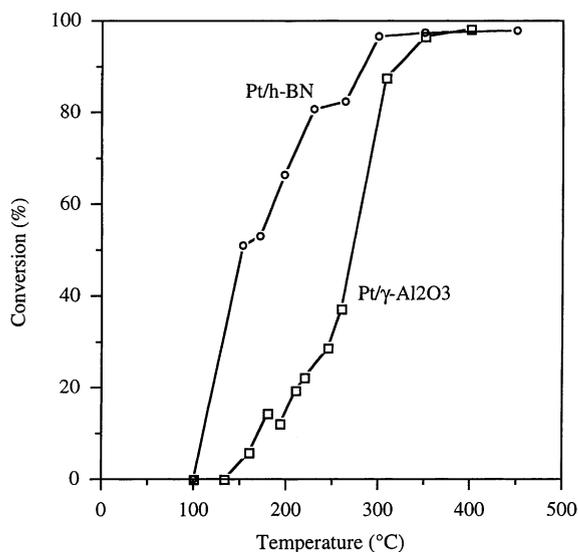
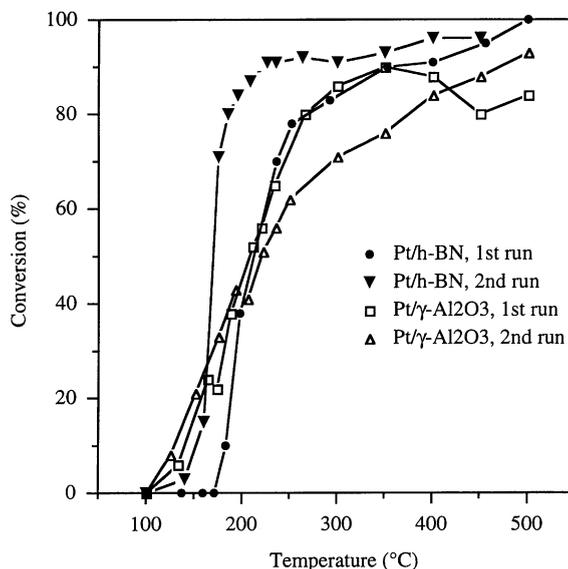


Fig. 3. XPS B 1s of h-BN.

GC/mass analysis of CPC gasoline vapor disclosed that its primary components were *iso*-pentane and *iso*-hexane, and its minor components included C<sub>4</sub> isomers, benzene and toluene. Fig. 4 shows the temperature dependencies of *iso*-hexane oxidation on Pt/h-BN and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively. Fig. 5 depicts the oxidation results of the gasoline volatile on

Fig. 4. Oxidation of *iso*-hexane (600 ppmv) on Pt/h-BN and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.Fig. 5. Oxidation of gasoline vapor on Pt/h-BN and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Pt/h-BN and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively. As shown in Figs. 4 and 5, the activity of Pt/h-BN was superior to that of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. In addition, the light-off temperature (50% conversion) of Pt/h-BN was 170°C, while that of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was approximately 260°C. Similar results were also found for the oxidation of gasoline vapor. In Fig. 5, initially the activities of Pt/h-BN and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were not noticeably distinguished and the light-off temperatures were near 210°C. After the reactor was cooled to room temperature, the second run reaction was re-started and the temperature increased to 500°C. During the second run reaction, both catalysts showed a significant difference. The light-off temperature of Pt/h-BN decreased to near 170°C and the oxidation quickly attained a conversion greater than 95% at 220°C, while the activity of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> declined. The light-off temperature of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> escalated slightly to 220°C, and temperatures greater than 500°C were required to achieve 90% conversion. While near complete oxidation of *iso*-hexane was achieved at 300°C with Pt/h-BN catalyst and at 350°C with Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (Fig. 4), only about 90% of gasoline vapor was oxidized at the similar temperatures with these two catalysts, respectively (Fig. 5). Complete oxidation of gasoline vapor was obtained only after the reaction temperature was raised to over 450°C in Pt/h-BN. Conceivably the demand for

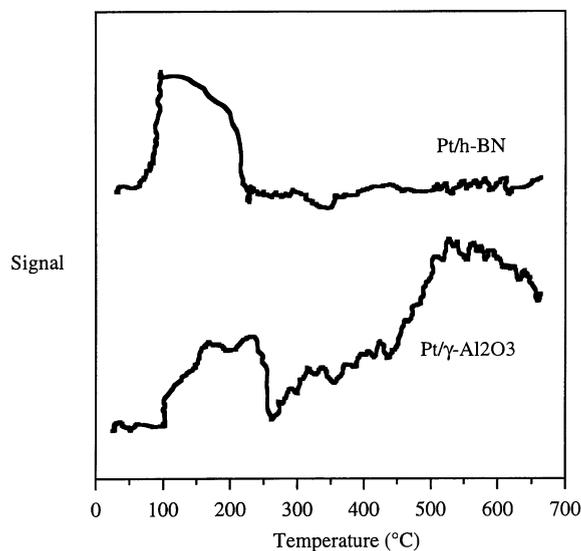


Fig. 6. TPR of Pt/h-BN and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

higher oxidation temperature may be attributed to the existence of aromatics in the gasoline vapor which generally are hard to be oxidized. In order to test the superior property of h-BN as catalyst support, the rest of the study was conducted with gasoline vapor as the feed which contained ~10 vol.% of light aromatics according to GC analysis.

The light-off temperatures were found to correlate well with the metal-oxygen bond energy of noble metals especially at lean VOC/air ratio [9]. Yao et al. reported that the dispersion phase of Pt oxide had a large interaction with  $\gamma$ -alumina when Pt loading was low. The deactivation of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> might be possible due to the dissolution of PtO<sub>2</sub> into the surface layer of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or the formation of a PtO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> complex [2]. This kind of metal-support interaction can significantly reduce the reactivity of adsorbed oxygen on Pt. Fig. 6 displays the TPR results of Pt/h-BN and Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, respectively. Only one reduction temperature was observed on Pt/h-BN near 100°C, while Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> gave two reduction temperatures, near 150°C and above 450°C. The TPR study of Hwang and Yeh indicated that for Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, various PtO<sub>x</sub> gave distinct reduction temperatures. The reduction temperature close to 150°C is due to PtO<sub>2</sub>, which gives less activity in VOC oxidation than PtO (reduced at near 100°C) does. Pt-aluminate is formed

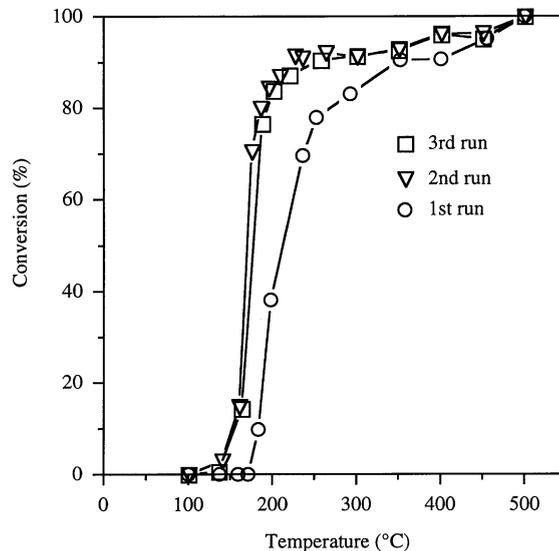


Fig. 7. The oxidation of gasoline vapor on Pt/h-BN.

at 500°C, which substantially reduces Pt activity [10]. Völter et al. found that metallic Pt were more active than Pt oxide complex in the oxidation of *n*-heptane [3]. Our support, h-BN, other than residual B–O bonds, virtually has no interaction with Pt. Moreover, akin to graphite, the benzene-like structure of h-BN may act as an electron donor to facilitate oxygen chemisorption by the Pt atom. During VOC oxidation, the surface of metallic Pt is covered either by PtO or chemisorbed oxygen, which are both highly reactive for oxidation. Therefore, the activity of Pt/h-BN is higher than that of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The activity duration of Pt/h-BN was further investigated to explain the increasing activity in the second run of oxidation. Fig. 7 depicts the oxidation of Pt/h-BN for two additional cycles. Notably, the activity was well maintained during the third run. The results indicated that, after the first oxidation, the Pt surface became more active, then was preserved thereafter. Fig. 8 displays the pretreatment effect in the oxidation activity. In order to distinguish either the thermal or oxidative effect, one of two kinds of pretreatment, N<sub>2</sub> or air at 300°C, was applied to the fresh catalysts prior to gasoline vapor oxidation, respectively. The catalyst of pretreatment in air gave the light-off temperature of approximately 170°C and attained 90% conversion near 200°C. They were very similar to the results of the

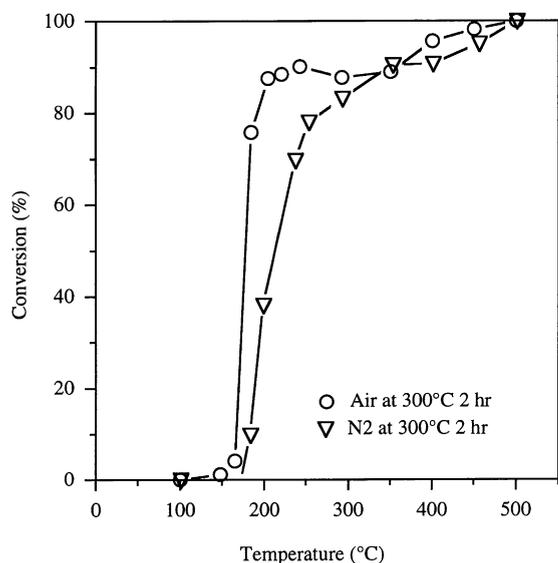


Fig. 8. The effect of pretreatment on the activity of gasoline oxidation of Pt/h-BN.

second run in Fig. 7. The Pt/h-BN with pretreatment in  $N_2$  gave low initial activity. Thermal  $N_2$  treatment cannot assist the PtO formation, thus yielding low initial activity. Therefore, in the second run of oxidation, that Pt/h-BN gave better activity than the first run was due to cleaner surface of Pt cluster as well as the formation of active PtO species during the VOC oxidation.

The anchorage of Pt on the h-BN surface via residual B–O bonds may not be as strong as that on  $\gamma\text{-Al}_2\text{O}_3$ . However, the experimental results in Tables 1 and 2 indicate that h-BN provides a moderate surface area, which can accommodate the Pt cluster and maintain its dispersion without sintering after oxidation reaction.

The life span of a catalyst is crucial for its industrial application. Fig. 9 demonstrates the long-term stability comparison of Pt/h-BN and Pt/ $\gamma\text{-Al}_2\text{O}_3$ . The oxidation was maintained at  $185^\circ\text{C}$  to study the deactivation of catalysts. Within 2 h, the conversions were quickly increased to 90 and 72% in Pt/h-BN and Pt/ $\gamma\text{-Al}_2\text{O}_3$ , respectively. The activity of the former was well sustained for 80 h, and showed no sign of deactivation. In fact, the conversion was slightly increased to 95% at the end of 80 h. In contrast, the conversion of Pt/ $\gamma\text{-Al}_2\text{O}_3$  began to decrease after 15 h, then gradually reduced to less than 60%. A less

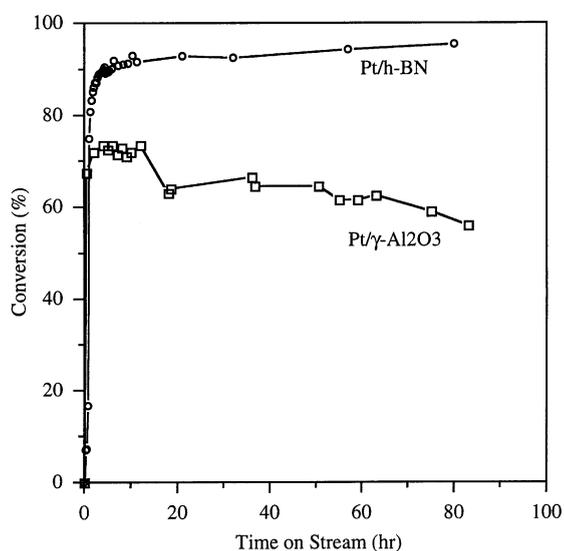


Fig. 9. The oxidation of gasoline vapor on Pt/h-BN and Pt/ $\gamma\text{-Al}_2\text{O}_3$  at  $185^\circ\text{C}$ .

active oxidic surface complex  $\text{Pt}^{\text{IV}}$  might be formed on the alumina surface resulting in the deactivation of Pt/ $\gamma\text{-Al}_2\text{O}_3$  [3] while no such effect occurred on h-BN surface. Although the apparent reaction temperature was only  $185^\circ\text{C}$ , the real temperature of local Pt site was likely much higher. The thermal conductivity of h-BN is higher than that of  $\gamma\text{-alumina}$  [11]. The Pt sintering may be minimized due to the elimination of hot spots on catalysts during deep oxidation.

The aforementioned findings indicate that h-BN provided a superior support for Pt in deep VOC oxidation. Unlike  $\gamma\text{-alumina}$ , there are virtually no acid sites on h-BN, thus the activity loss due to coking can be minimized. An additional advantage of h-BN is its high-temperature potential (greater than  $800^\circ\text{C}$ ) because there is no phase transformation phenomenon as occurs with  $\gamma\text{-Al}_2\text{O}_3$  or other oxides. Consequently, several undesirable factors affecting the traditional oxide support, such as coking and metal–support interaction, are absent and would not deactivate Pt/h-BN catalyst.

#### 4. Conclusion

This study showed the favorable findings of VOC incineration employing h-BN supported Pt catalysts.

The light-off temperature of gasoline vapor was as low as 170°C. The oxidation conversion achieved more than 90% near 200°C. Furthermore, Pt/h-BN activities can be maintained and endure longer than those of traditional Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Notably, boron nitride exhibits superior properties, which include chemical inertness, thermal stability, thermal conductivity and minimum metal–support interaction. Low crystalline h-BN provides a moderate surface area that can accommodate dispersed phase noble metals, while still preserves the unique characteristics. Boron nitride is a promising support for catalysts. The use of h-BN will become a frontier in catalysis.

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