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Deep Oxidation of Methanol Using a Novel Pt/Boron Nitride Catalyst

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Deep oxidation of methanol was conducted using a novel Pt/BN catalyst in a steady-state-flow reactor. Hexagonal boron nitride (BN) is a graphitelike material in powder form with a specific surface area of 49 m^2/g. A catalyst with 0.37 wt % Pt was prepared by the incipient wetness method using H_2PtCl_6 as a precursor dissolved in methanol. The reaction temperature ranged from −10 to 200 °C. The concentration of methanol varied from 1000 to 4000 ppmv, while the oxygen varied from 5 to 80% and was balanced with nitrogen. The volume hourly space velocity was approximately 50 000 h^{-1}. Experimental results showed that a 50% methanol conversion could be achieved at room temperature (20 °C), reaching 95% conversion at 75 °C, while Pt/Al_2O_3, Dash 220 (a commercial Pt/alumina catalyst), and PtPd/CeO_2/Al_2O_3 catalysts required considerably higher temperatures under the same conditions. The high oxidation activity of Pt/BN was attributed to the weak Pt−O bonding of the Pt clusters on the BN surface, which led to high oxidizing reactivity. Regression analysis revealed that the reaction order of methanol was 1, while that of oxygen was −0.6. A mechanism of the Langmuir−Hinshelwood model was established based on the experimental results. Kinetic analysis suggested that the methanol adsorption on Pt would be the rate-limiting step on the Pt/BN catalyst.

Introduction

Materials traditionally used as supports are insulating oxides such as SiO_2, γ-Al_2O_3, silica−alumina, and various zeolites.[1] These oxides possess low thermal conductivity, causing sintering of the supported metal on hot spots, numerous acidic and basic sites, and the coverage of the catalyst with water at low temperature due to its hydrophilic surface. The graphitelike hexagonal boron nitride (BN) is the most stable isomer of BN under ambient conditions.[2] BN has high thermal conductivity, temperature stability, acid−base resistance, and appropriate chemical inertness. Furthermore, BN is hydrophobic, thus preventing moisture condensation on its surface.

Our laboratory recently investigated Pt catalysts supported on hexagonal BN.[3,4] The Pt/BN catalysts were compared with Pt/γ-Al_2O_3 for the deep oxidation of gasoline vapor. The oxidative conversion of gasoline vapor rose to 90% at approximately 150 °C. In contrast, the light-off temperature (for 50% conversion) of Pt/γ-Al_2O_3 with the same pretreatment was at 250 °C. The Pt/BN catalyst remains active for 80 h, meanwhile the activity of Pt/γ-Al_2O_3 declined continuously with time when the temperature was fixed at 185 °C.[3] The BN surface bonds more weakly to Pt particles than does γ-Al_2O_3, indicating a weaker interaction between the Pt and the support. This weaker bonding between the support and the Pt particles allows the particles to remain in a reduced state more easily. The reduced state of Pt particles on Pt/BN causes a weaker Pt−O bond on the surface of Pt to supply more reactive oxygen atoms and thus promote catalytic oxidation.[4] Previous works have concluded that Pt/BN outperforms the traditional oxide-supported Pt catalysts in life and activity.

Methanol is an alternative fuel for internal combustion engines, with the potential simultaneously to increase the octane number and reduce air pollution. However, unburned methanol vapor released from vehicle exhaust pipes is a health hazard. Owing to the low temperature in methanol-fuel internal-combustion engines, a catalyst that is active under low temperature is extremely important, particularly when the operating temperature is lower than the dew point of exhaust gas in the catalytic converter. This study demonstrates the deep oxidation of methanol at extremely low temperature using a novel Pt/BN catalyst.

Experimental Section

(a) Catalysts. The hexagonal BN powder was purchased from High Performance Material Inc., Taiwan. γ-Alumina (γ-Al_2O_3), a commonly used support, from Merck (St. Louis, MO) was used to prepare Pt/γ-Al_2O_3 catalyst. The average particle diameters of the BN and γ-Al_2O_3 supports were 10 and 180 μm, respectively. Two commercial catalysts were used for comparison. A volatile organic compound (VOC) catalyst, PtPd/CeO_2/Al_2O_3, was obtained from KJ Environmental Technology Co. (Taiwan). The total Pt and Pd loading of PtPd/CeO_2/Al_2O_3 is around 1 wt %, being used as supplied by the manufacturer. Another combustion catalyst, Dash 220, was purchased from N. E. Chemcat Corp. (Tokyo, Japan). Dash 220 is an alumina-supported Pt catalyst with a specific surface area of 150 m^2/g and was used as supplied by the manufacturer.

Platinum catalysts with 0.37 wt % loading were prepared by the incipient-wetness method. The precursor salt, $H_2PtCl_6 \cdot 6H_2O$, which contained approximately 40 wt % platinum, was purchased from Acros Organics (Geel, Belgium). Methanol was found to be an effective solvent that could soak BN and dissolve the precursor salt. The catalysts were reduced in a flow of 30 mL/min of a 20% H_2/N_2 mixture at 300 °C for 2 h, with the

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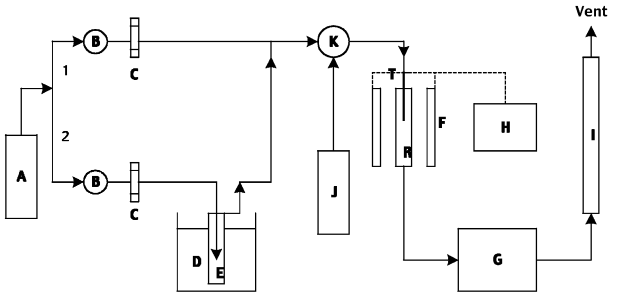

Figure 1. Schematic of the reactor system (A, air cylinder; B, pressure gauge; C, rotameter; D, water bath; E, methanol saturator; F, furnace; G, gas chromatograph; H, furnace controller; I, bubble meter; J, pretreatment gas; K, six-way valve; R, reactor; T, thermocouple).

temperature being increased from room temperature to 300 °C at 10 °C /min, then cooled to room temperature, and stored in a desiccator for later use. The specific surface areas of the catalysts were measured by N_2 adsorption, using the Brunauer−Emmett−Teller equation. The detailed characteristics of Pt/BN catalysts have been described elsewhere.[4]

The acidity of BN and Al_2O_3 supports was studied using the temperature-programmed desorption (TPD) of pyridine. Fresh support (0.2 g) was pretreated under a nitrogen flow at 400 °C for 1 h to remove adsorbed impurities and then cooled to near 50 °C. Following saturation with pyridine vapor carried out by a nitrogen stream for 30 min, the support was purged with Ar flow, and then the temperature was raised to 600 °C at 10 °C/min.

(b) Catalytic Oxidation. Figure 1 schematically illustrates the reaction system. An O_2/N_2 stream through a methanol saturator was mixed with another O_2/N_2 stream. The concentration of methanol in the feed was regulated in the range 1000−4000 ppmv by adjusting the saturator temperature. Three gas cylinders provided three oxygen concentrations balanced with nitrogen, namely, 5, 20, and 80%, respectively. The mixture passed through the reactor at 200 mL/min, representing a volume hourly space velocity of 50 000 h^{-1}. 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 the reaction temperature and control the furnace. The reaction temperature varied from −10 to 200 °C, and the subambient reaction temperature was maintained via chilled water circulation. The reactor was switched to a tubular furnace for temperatures above ambient temperature. The catalyst was heated 2 h at 300 °C under an air stream in the reactor and then cooled to room temperature before introducing methanol. All catalytic oxidations were performed in the steady-state condition and started at a temperature that ensured zero conversion of the methanol. The concentration of methanol was measured at least two or three times in the steady state at each temperature using an online sampling loop in an HP GC6890. The thermal conductive and flaming ion detectors were connected in series so that hydrocarbon and non-hydrocarbon species could be measured simultaneously. Moreover, separation of H_2O, CO_2, and most light hydrocarbons was accomplished using an HP-PLOT Q 30 m capillary column. Only water and carbon dioxide were detected in the methanol oxidation. Furthermore, the carbon balance was examined and found to be within a relative error of less than 10%. The conversions of oxidation were calculated based on the product, CO_2. The reaction was also conducted under various flow rates to test the influence of mass-transfer resistance on the catalyst. No significant rate change was noted, meaning that the mass-transfer limitation was negligible.

Table 1. Specific Area of Catalysts

	catalyst (m^2/g)			
	Pt/BN	Pt/Al_2O_3	PtPd/CeO_2/Al_2O_3	Dash 220
fresh	48.5	112.9	102.3	150.0[a]
reaction[b]	49.0	114.3	101.6	

[a] Provided by N. E. Chemcat Corp. [b] Methanol oxidation: total reaction time near 10 h, 30 min at maximum temperature, 140 °C.

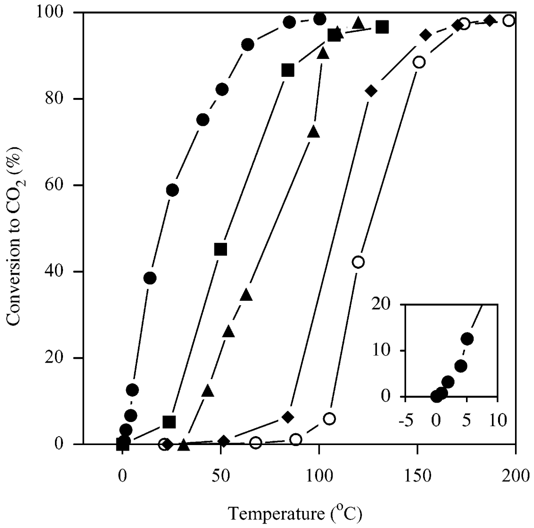

Figure 2. Oxidation of methanol using various catalysts (2000 ppmv, 20% O_2): ●, Pt/BN; ■, PtPd/CeO_2/Al_2O_3; ▲, Dash 220 (N. E. Chemcat Corp.); ◆, Pt/Al_2O_3; ○, BN.

Results and Discussion

Table 1 lists the specific surface areas of the catalysts. The Pt/BN has the lowest specific surface area among the four catalysts, at near 50 m^2/g. The specific surface areas of Pt/BN, Pt/Al_2O_3, and PtPd/CeO_2/Al_2O_3 following the reaction with methanol at a maximum 140 °C closely resemble those of fresh catalysts. The Pt dispersion of the catalyst was measured by static hydrogen chemisorption.[3,4] The Pt/γ-Al_2O_3 catalyst shows a Pt dispersion of around 30%. Meanwhile, the Pt/BN catalyst, with lower specific support surface areas, gives lower dispersions near 20%.

Figure 2 presents the temperature dependencies of methanol oxidation to CO_2 on Pt/BN, PtPd/CeO_2/Al_2O_3, Dash 220, Pt/γ-Al_2O_3, and blank support BN, respectively. The pure BN support gives very extremely low activity, indicating that Pt is the primary active site in such an oxidation reaction. Conversions increase steeply with temperature in all catalysts. As shown in Figure 2, the activity of Pt/BN was superior to that of PtPd/CeO_2/Al_2O_3, Dash 220, and Pt/γ-Al_2O_3. Table 2 summarizes the light-off temperatures of the four catalysts. Generally, the light-off temperature of a VOC catalyst is defined as the temperature at which conversion reaches 50%, assigned as T_{50}. The lower T_{50}, the higher the activity and the better the catalyst is. T_{50} of Pt/BN was near 20 °C, while those of PtPd/CeO_2/Al_2O_3, Dash 220, and Pt/γ-Al_2O_3 were approximately 55, 75, and 110

Table 2. Light-Off Temperatures of Methanol Oxidation[a]

catalyst	T_{50} (°C)	T_{95} (°C)
Pt/BN	20	75
PtPd/CeO_2/Al_2O_3	55	110
Dash 220	75	110
Pt/Al_2O_3	110	155

[a] T_{50} (°C): temperature at 50% conversion to CO_2. T_{95} (°C): temperature at 95% conversion to CO_2.

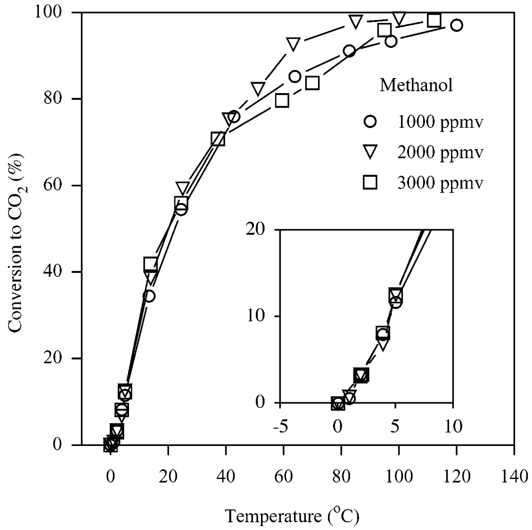

Figure 3. Effect of the methanol concentration in oxidation on a Pt/BN catalyst (20% O_2).

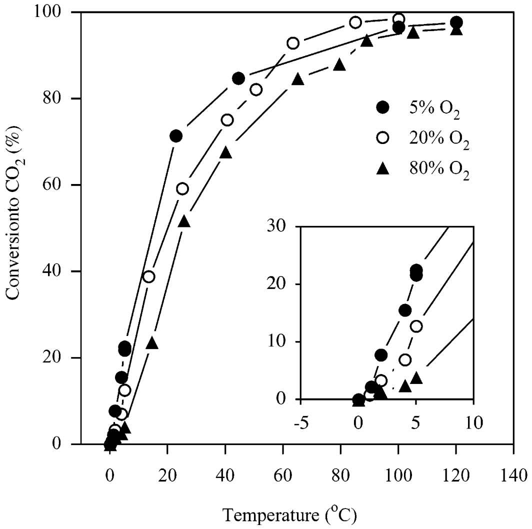

Figure 4. Effect of the O_2 concentration in methanol oxidation on a Pt/BN catalyst (2000 ppmv methanol).

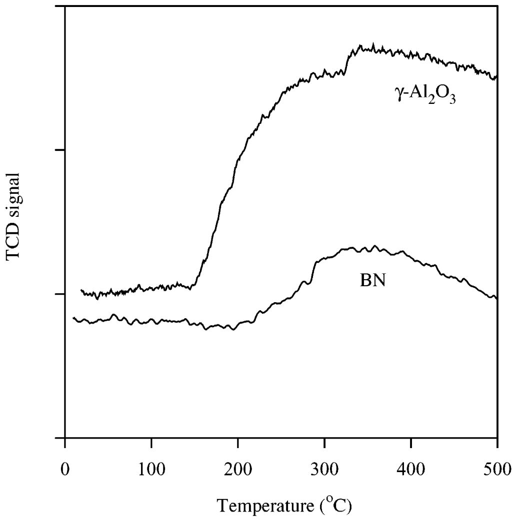

Figure 5. TPD of pyridine on supports.

°C, respectively. Notably, methanol conversion reaches 95% at ∼75 °C on Pt/BN. However, temperatures exceeding 110 °C are required to achieve 95% conversion on Dash 220 and PtPd/CeO_2/Al_2O_3.

Figures 3 and 4 show the concentration effects of methanol and oxygen on Pt/BN, respectively. Differences in the methanol concentration were observed to have only a minor influence on conversion. It may be that the range of methanol concentrations used in this study was too narrow to reveal the differences. Oxygen had a negative effect on the conversion under the experimental conditions. Methanol conversion decreased with increasing oxygen concentration at the same temperature, especially at low conversion levels. The reason is that oxygen is more competitively adsorbed on the active Pt sites than methanol. Thus, the number of active sites for methanol adsorption is insufficient, resulting in lowered methanol conversion at high oxygen concentrations.

Volter et al.[5] and Aryafar and Zaera[6] both conclude that hydrocarbon oxidation reactions over platinum occur on reduced sites more easily than on oxidized ones. The Pt particles on Pt/BN are more easily maintained in their reduced state, as was concluded in the previous characterization, a result that is believed to be the most important in causing the difference between the activities of Pt/BN and Pt/γ-Al_2O_3.[4] Weaker bonding between Pt and ad-oxygen on Pt/BN is thought to be responsible for supplying the more reactive surface oxygen atoms in the deep oxidation of methanol. Moreover, the low activity of Pt/γ-Al_2O_3 is believed to result from the strong bonding between Pt and ad-oxygen and the presence of a more residual PtO_xCl_y complex on the surface of the support. Consequently, the ad-oxygen on the Pt/BN is more reactive than that on Pt/γ-Al_2O_3.

The acidity of the catalyst can be generally studied by TPD using a basic adsorbate. Figure 5 displays the TPD spectra of pyridine on BN and γ-Al_2O_3. The desorption peak of γ-Al_2O_3 is high and widespread, ranging from 150 to over 500 °C, while that of BN is low and significantly narrower, ranging from 200 to near 500 °C. The amount of pyridine adsorption indicates that the quantity of acidic sites of BN is significantly less than that of γ-Al_2O_3. The acidic strength of BN is also weaker than that of γ-Al_2O_3. Hinz et al. suggested that a basic support, such as MgO, was more favorable than an acidic support (e.g., γ-Al_2O_3) in methanol oxidation using supported Pt catalysts.[7] The acid−base character of the support is an important factor influencing the performance of supported Pt in methanol oxidation at low temperature. Therefore, T_{50} of Pt/BN is considerably lower than that of Pt/γ-Al_2O_3, despite the dispersion of Pt on BN (20%) being lower than that on γ-Al_2O_3 (30%).

Our previous work found a slight decrease in the Pt dispersion following aromatics oxidation at high temperatures (>300 °C) on Pt/BN.[3,4] However, the weak bonding strength between the BN support and Pt particles on Pt/BN is believed to be sufficient to fix Pt particles on the surface, particularly at low-temperature methanol oxidations.

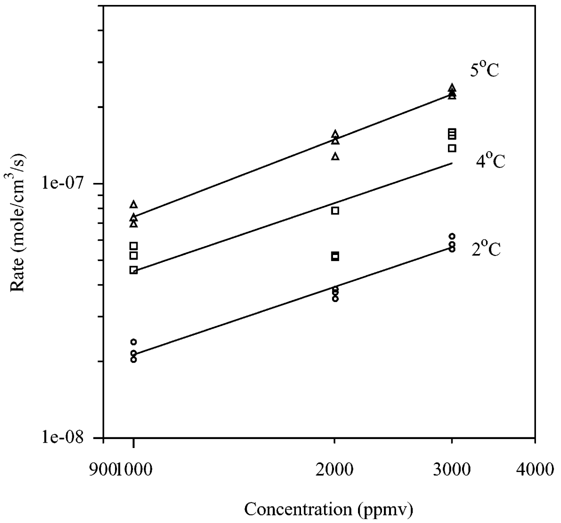

Figure 6. Reaction rates of various methanol concentrations in 20% O_2 on a Pt/BN catalyst.

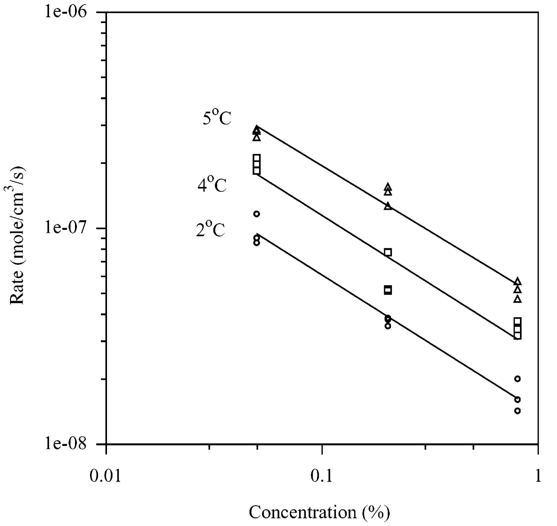

Figure 7. Reaction rates of various O_2 concentrations in 2000 ppmv methanol on a Pt/BN catalyst.

Kinetic Analysis. The intrinsic kinetics are ensured by only using the low conversion (<10%) data, in which diffusion limitations can be excluded. The apparent activation energy of methanol oxidation on Pt/BN is calculated to be 267 kJ/mol from an Arrhenius plot. The value of the apparent activation energy also suggests that the reaction is in the kinetic control region. The rate equation of methanol oxidation can be expressed by the concentrations of methanol and oxygen using a power law. Moreover, the exponents of methanol and oxygen can be estimated via regression analysis. Figures 6 and 7 display the rates versus concentrations of methanol and oxygen, respectively. The kinetic order of methanol is near 1, while that of oxygen is −0.6, based on the slopes calculated with the least-squares method. Equation 1 is the rate equation of methanol oxidation.

$$-r = k'[CH_3OH][O_2]^{-0.6} \tag{1}$$

The kinetics of methanol oxidation were further analyzed using the Langmuir−Hinshelwood model. Our experimental results showed that only water and carbon dioxide were produced. Formaldehyde or dimethyl ether might be intermediate species,[8] but neither was detected in the present experiment. Notably, only the adsorptions of methanol and oxygen were assumed on the Pt sites. Consequently, three elementary steps were proposed to describe the methanol oxidation on the Pt surface.

$$CH_3OH + i \xrightarrow{k} CH_3OH{-}i \tag{2}$$

$$O_2 + 2i \xrightarrow{k_2} 2O{-}i \tag{3}$$

$$CH_3OH{-}i + 3O{-}i \xrightarrow{k_3} CO_2 + 2H_2O + 4i \tag{4}$$

The rate-determining step (RDS) could be any one of the above three steps. Each RDS can derive an individual rate equation. According to the experimental results, the adsorption of methanol (eq 2) was found to be the most likely candidate for the RDS because the orders of methanol and oxygen were consistent with the experimental results. The rate equation is derived and presented in eq 5 where C_t denotes the total number of

$$-r = \frac{C_t k[CH_3OH]}{1 + \sqrt{K_2[O_2]} + \dfrac{[CO_2][H_2O]^2}{K_3[\sqrt{K_2[O_2]}]^3}} \tag{5}$$

active sites that are constant for a given catalyst. K_2 and K_3 are reaction equilibrium constants in eqs 3 and 4, respectively. The denominator of eq 5 can be reduced to eq 6 because the concentrations of H_2O and CO_2 are extremely small (ppmv level) compared to those of O_2 (∼5−80%).

$$-r = \frac{C_t k[CH_3OH]}{1 + \sqrt{K_2[O_2]}} \tag{6}$$

The numerical value of $K_2[O_2]$ would exceed 1 because the dissociation adsorption (K_2) is significant in Pt active sites, and the concentration of O_2 is also high in the present experimental condition. Consequently, eq 6 can be further reduced to eq 7. Finally, the kinetic order of methanol is first order and oxygen becomes negative half order, both of which kinetic orders agree closely with the experimental results (eq 1).

$$-r = C_t k\sqrt{K_2}[CO_3OH][O_2]^{-0.5} \tag{7}$$

The negative order of the oxygen concentration indicates that oxygen inhibits the reaction rate. The adoxygen may cover most of the Pt active sites under high oxygen concentration (10−80%) in our experimental conditions. Therefore, few Pt active sites are available for the methanol adsorption. That is also the reason the RDS is the adsorption of methanol (eq 2).

Conclusion

This study presented favorable findings regarding methanol combustion employing BN supported Pt catalysts. Notably, the light-off temperature of methanol vapor was as low as 20 °C. Moreover, oxidation conversion exceeded 95% at near 75 °C. The weaker bonding between BN and Pt particles allow the Pt particles to remain in a reduced state more easily. The reduced state of the Pt particles on Pt/BN causes a weaker Pt−O bond on the surface of Pt particles, providing highly reactive oxygen and thus promoting methanol oxidation. BN exhibits superior properties, including chemical inertness, thermal stability, thermal conductivity, and minimum metal−support interaction. Accordingly, BN is a promising support for a deep-oxidation catalyst.

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