

# Highly Active Pt/BN Catalysts for Propane Combustion: The Roles of Support and Reactant-Induced Evolution of Active Sites

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Supporting Information

ABSTRACT: The Pt catalysts supported on hexagonal BN (Pt/BN) are highly active and stable for propane combustion, with the highest specific reaction rate of 92.3  $\mu$ mol  $g_{Pt}^{-1}$  s<sup>-1</sup> and turnover frequency of 0.037 s<sup>-1</sup> obtained on a 0.2Pt/BN catalyst at 220 °C. The Pt oxide in the catalyst could be partially reduced to the metallic state by propane during the reaction, which is beneficial for the improvement of activity, indicating that metallic Pt might be the active sites. The highly dispersed Pt particles stabilized at the grain boundary of BN could be more easily reduced in the reaction than those on the surface and thus are more active. Moreover, kinetic investigation reveals that the apparent activation energy of the Pt species at the grain boundary (111.6  $\pm$  8.0 kJ mol<sup>-1</sup>) is much lower than that on the surface  $(172.4 \pm 16.5 \text{ kJ mol}^{-1})$ , suggesting different reaction



pathways on these catalysts and the possible participation of the grain boundary of the BN support in the reaction.

**KEYWORDS:** hexagonal boron nitride, propane, catalytic combustion, grain boundary, active sites

#### 1. INTRODUCTION

Alkanes are one of the main volatile organic compounds (VOCs) pollutants, which are produced from the emission of industrial exhaust of coal processing, petroleum refining, and natural gas processing as well as the incomplete combustion of fossil fuels such as gasoline and diesel.<sup>1-4</sup> Catalytic combustion is considered to be one of the most efficient routes for the abatement of the alkanes due to its advantages such as higher efficiency and lower energy cost compared to direct incineration. However, the catalytic combustion of alkanes especially light alkanes (C1-C3) remains challenging because of their inert chemical nature and thus high reaction temperature is usually required for the activation and cleavage the strong C-H bond. Highly efficient catalyst systems have been developed for the combustion of light alkanes. Taking the catalytic combustion of propane as an example, the currently employed catalysts include supported noble metals such as Pt, Pd, Au and Ru,<sup>5-14</sup> transition metal oxides such as Cu, Mn, Co, Fe, Ni, and Ce oxides  $^{15-29}$  and structured oxides such as perovskites and spinel oxides.  $^{30-35}$ 

Supported Pt catalysts have been widely applied in propane combustion, and some valuable insights have been reported. One important finding is that the support could significantly affect the catalytic performance through the support-related modification of the properties of the Pt species. Yazawa et al.<sup>36</sup> compared the catalytic performance of supported Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/MgO, and Pt/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> catalysts. They found that the basicity-acidity properties of the supports affected the oxidation states of the Pt species, namely, the Pt species on the acidic support (i.e.,  $Al_2O_3$ ) were less oxidized than those on the basic support (i.e., MgO), which accounted for their high activity in propane combustion. Wu et al. also found that one of the promoting roles of WO<sub>3</sub> in the Pt/TiO<sub>2</sub> catalyst was the maintenance of the metallic state of platinum by providing more stable Bronsted acid sites.<sup>37</sup> Enterkin et al.<sup>38</sup> conducted propane combustion on a Pt/SrTiO<sub>3</sub> catalyst, and the authors concluded that the maintenance of a Pt/PtO core/shell structure during operating conditions was vital for the improvement of the activity.

The above findings in literature reflect the importance of the support for Pt catalysts in propane combustion. In recent years, boron nitride (BN) has attracted much attention due to its properties such as high chemical stability and high thermal conductivity. Also, the BN materials have been widely applied in catalysis, such as VOCs combustion,  $^{39-41}$  selective hydro-genation,  $^{42}$  selective oxidation,  $^{43,44}$  photocatalysis  $^{45}$  and CO oxidation  $^{46}$  The variance of genation,<sup>42</sup> selective oxidation,<sup>43,44</sup> photocatalysis<sup>45</sup> and CO oxidation.<sup>46</sup> The unique surface chemical and electronic properties of BN materials are also dependent on their morphologies (i.e., nanosheet, nanoribbon and nanotube), which has been recently reviewed by Pakdel and co-workers.<sup>4</sup> Moreover, the importance of the defects in BN material has been recognized. For instance, Grant et al.44 attributed high activity of hexagonal BN (h-BN) in dehydrogenation of propane to the formation of peroxo species (>B-O-O-N < )

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Table 1.	Physical	Properties	and Cat	lytic Resul	lts of Pt/	'BN Catalys	ts
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sample	surface area / $m^2 \ g^{-1}$	Pt particle size <sup><i>a</i></sup> / nm	Pt dispersion <sup>b</sup> / %	$C_3H_8 \text{ conv.}^c$ / %	reaction rate <sup><i>d</i></sup> / $\mu$ mol $g_{Pt}^{-1}$ s <sup>-1</sup>	$TOF^{d} / \times 10^{-3} s^{-1}$
0.2Pt/BN	17.6	$2.1 \pm 0.5$	49.0	9.3	92.3	36.8
0.5Pt/BN	19.1	$2.1 \pm 0.5$	48.5	15.6	87.6	35.2
1Pt/BN	18.9	$2.0 \pm 0.5$	46.5	30.5	65.2	27.3
2Pt/BN	20.5	$2.2 \pm 0.5$	45.9	45.0	44.6	19.2
5Pt/BN	19.7	$2.4 \pm 0.5$	33.4	48.3	21.8	12.7
0.5Pt/BN-H	19.2	$1.5 \pm 0.5$	45.8	8.0	31.7	13.4

<sup>*a*</sup>Determined by TEM. <sup>*b*</sup>Determined by H<sub>2</sub> chemisorption. <sup>*c*</sup>C<sub>3</sub>H<sub>8</sub> conversions taken at reaction time of 3 h at reaction temperature of 220 °C. <sup>*d*</sup>Reaction rates and TOF values were calculated under kinetic region with propane conversion level less than 10% (detailed results were summarized in Table S1).

at the boron nitride boundary. In VOCs combustion, Wu and co-workers reported that the supported Pt/h-BN were much more active than the traditional  $Pt/Al_2O_3$  catalyst for the catalytic combustion of benzene, methanol and volatile gasoline.<sup>39,41,48</sup> The authors assigned the excellent performance of the Pt/h-BN catalysts to the presence of metallic Pt species, which could supply more active adsorbed oxygen atoms for the oxidation reaction.

It seems that BN is a promising support for supported catalysts. Therefore, in this work, we prepared a series of Pt catalysts supported on h-BN and tested them for catalytic combustion of propane. It is found that these catalysts are much more active than those on conventional oxides such as  $Al_2O_3$ . Detailed characterizations results reveal that the h-BN support plays an important role in governing the properties of the Pt species, which in turn exert significant impacts on the catalytic behaviors. Also, reactant-induced evolution of active species is observed during the reaction process.

#### 2. EXPERIMENTAL SECTION

**2.1. Catalyst Preparation.** The supported Pt/BN catalysts were prepared using an impregnation method. In a typical synthesis, 1 g of commercial hexagonal BN support (h-BN, Aladdin, 99.9%,  $S_{BET} = 18.5 \text{ m}^2 \text{ g}^{-1}$ ) was impregnated with a proper amount of aqueous solution of Pt(NO<sub>3</sub>)<sub>2</sub> (2 mg mL<sup>-1</sup>). After the suspension was kept at room temperature for 2 h, the water was evaporated at 90 °C under stirring. The solid was dried at 100 °C overnight and then calcined at 500 °C in static air for 4 h. The resulting catalysts were labeled as *x*Pt/BN, where *x* is the nominal weight percentage of Pt in the catalyst.

A 0.5Pt/BN-H catalyst was prepared using the same impregnation method as described above, except that a mixture of 2.5 mL of aqueous solution of  $Pt(NO_3)_2$  (2 mg mL<sup>-1</sup>) and 10 mL of aqueous solution of nitric acid (HNO<sub>3</sub>, 65–68 wt %) was impregnated with 1 g of the BN support. The obtained catalyst was denoted as 0.5Pt/BN-H.

**2.2. Catalyst Characterizations.** The specific surface areas of the catalyst were measured by  $N_2$  sorption at 77 K on a BK200C surface area analyzer. The catalysts were dried at 110 °C overnight and degassed at 200 °C for 4 h before the measurement. The surface area was calculated by the Brunauer–Emmet–Teller (BET) method.

The powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Bruker's D8 Advance diffractometer employing Cu K $\alpha$  radiation, which was operated at 40 kV and 40 mA.

Transmission electron microscopy (TEM) images of Pt/BN catalysts were obtained using a JEOL JEM-2100F electron microscope operated at 200 kV.

The Pt dispersion in the catalyst was determined by  $H_2$  chemisorption on a Micromeritics Autochem II equipment. Fifty mlligrams of the catalyst (100 mg for the samples with Pt contents of 0.2 and 0.5 wt %) was loaded in the U-tube and prereduced with 5 vol %  $H_2$  + 95 vol % Ar (30 mL min<sup>-1</sup>) at 400 °C for 1 h, and then it was purged with Ar (30 mL min<sup>-1</sup>) for another 1 h. After the sample was cooled to room temperature in Ar, a high-purity  $H_2$  pulse was introduced. The Pt dispersion was calculated on the basis of the equation Pt:H = 1:1.

Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) profiles of the catalysts were carried out in a fixed-bed reactor equipped with a thermal conductivity detector (TCD). Fifty milligrams of the sample was placed in a tubular quartz reactor (i.d. = 6 mm). After the sample was pretreated in 10% O<sub>2</sub> + 90% N<sub>2</sub> at 300 °C for 1 h to remove the adsorbed H<sub>2</sub>O and the surface carbonates, a gas mixture of 5% H<sub>2</sub>+ 95% N<sub>2</sub> with a flow rate of 30 mL min<sup>-1</sup> was introduced, and the sample was heated from room temperature to 400 °C at a heating rate of 10 °C min<sup>-1</sup>. The reduction of CuO powder with a known amount was used to calculate hydrogen consumption.

X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250Xi system equipped with monochromatic Al  $K\alpha$  X-rays to investigate the surface compositions and oxidation states of the elements. Carbonaceous C 1s line (284.8 eV) was used as the reference to calibrate the binding energies.

**2.3. Catalytic Testing.** The catalytic activities of samples for deep oxidation of propane were tested in a fixed-bed reactor. Fifty milligrams of the catalyst (60–80 mesh) diluted with 150 mg of quartz sand with same size was placed in a tubular quartz reactor (i.d. = 6 mm). The gas mixture was composed of 0.2%  $C_3H_8$ , 2%  $O_2$  and  $N_2$  in balance with a total flow rate of 67 mL min<sup>-1</sup>, which corresponded to a mass space velocity (S.V.) of 80 000 mL  $g_{cat}^{-1}$  h<sup>-1</sup>. To compare the effect of pretreatment on the catalytic behaviors of the catalyst, the calcined 2Pt/BN catalyst was prereduced a flow of H<sub>2</sub> (5 vol % H<sub>2</sub> balanced with N<sub>2</sub>, total flow rate of 30 mL min<sup>-1</sup>) at 300 °C for 1 h before reaction. The reactants and products were analyzed online by a gas chromatograph (GC) equipped with a TCD. The propane conversion was calculated by the equation:

$$\text{conversion} = ([C]_{\text{in}} - [C]_{\text{out}}) / [C]_{\text{in}} \times 100\%$$

where  $[C]_{in}$  and  $[C]_{out}$  were the inlet and outlet concentrations of propane, respectively. The carbon balance was close to 100  $\pm$  3%, and no byproducts other than CO<sub>2</sub> and H<sub>2</sub>O were detected.

Kinetics were conducted in kinetic region at differential reaction mode (with propane conversion less than 15%). The absence of mass and heat transfer limitations were verified, which includes Weisz–Prater criterion ( $C_{\rm WP}$ ) for internal diffusion, Mears' criterion ( $C_{\rm M}$ ) for external diffusion , and Mears' criterion ( $C_{\rm M}$ ) for heat transfer (see Supporting Information for detailed calculation). The reaction orders of propane and oxygen were measured at high O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> ratio, with propane partial pressure range of 0.202–0.535 kPa and oxygen partial pressure range of 4.053–9.119 kPa.

## 3. RESULTS AND DISCUSSION

**3.1. Characterizations of the Pt/BN Catalysts.** Table 1 lists the physical properties of Pt/BN catalysts. The catalysts have similar surface areas  $(17.6-20.5 \text{ m}^2 \text{ g}^{-1})$ . Note that the actual Pt contents in the catalysts could not be determined by X-ray fluorescence (XRF) technique due to the undetectable boron and nitrogen elements; therefore, the nominal Pt values are taken as the actual contents, and the errors could be acceptable because of the impregnation method for the catalyst preparation.

Figure 1 shows the XRD patterns of the Pt/BN catalysts. Typical diffraction peaks at  $2\theta$  of 26.8, 41.6, 43.9, 50.1, 55.1,



Figure 1. XRD patterns of Pt/BN catalysts with different Pt contents.

75.9, and  $82.2^{\circ}$  reflect the characteristics of hexagonal BN (JCPDS No. 34-0421). No observable diffractions due to Pt species could be detected, indicating that the Pt species are highly dispersed in the catalysts.

The morphologies of the catalysts were characterized by HRTEM, and the images are shown in Figure 2. The h-BN support has a sheet-like structure with a smooth surface. The Pt particles are preferentially deposited at the grain boundary of the support at low Pt loadings (<2 wt %, Figure 2a,b,d,e). When the Pt loading is high (5 wt %, Figure 2f), the Pt species tend to disperse on the surface. Such preferential deposition of metal species at the grain boundary of h-BN was also observed on the Pt/BN and Au/BN catalysts<sup>41,49</sup> because of the different properties of the h-BN surface and boundary. The imperfect crystallinity of the h-BN grain boundary leads to aligned dislocation and possible homoelemental bonding (i.e., B–B or N–N bonding), which thus carries charges at the grain boundary.<sup>47</sup> In the case of N-rich boundaries, the negative charges could attract and stabilize the Pt<sup>2+</sup> cations in the precursors, which could explain the observed preferential deposition of Pt particles at h-BN grain boundary. Lin et al.<sup>41</sup> also proposed that the terminal oxygen species (a B–O bond) at the h-BN boundary (edge region) may serve as anchoring sites for the Pt ions. Such defect-induced stabilization of metal species on h-BN is also clarified by Lin et al.,<sup>50</sup> based on their density functional theory calculations. The authors investigated various metal doped h-BN nanosheets (M = Cu, Ag, Au, Pt, Rh, Pd, Fe, Co, and Ir) and concluded that the strong interaction between the metal atoms and defect sites in h-BN (i.e., boron vacancy and nitrogen edge) made the metal doped h-BN nanosheets stable under high temperatures. Besides, it seems that the capacity of the boundary region is limited because of its low surface area, and the metal species are enforced to be deposited on the surface at high loadings. It is interesting to find that the 0.5Pt/BN-H shows different Pt distributions (Figure 2c). Compared with the 0.5Pt/BN (Figure 2b), the 0.5Pt/BN-H does not show preferential deposition of Pt at the BN grain boundary; instead, the Pt particles disperse on the BN surface. This could be possibly explained by that the negative charges on the h-BN grain boundary could be neutralized by protons in HNO<sub>3</sub> during the preparation process, and the anchoring sites at the boundary are no longer available for the Pt<sup>2+</sup> cations. The Pt particle size distribution could be calculated on the basis of the HRTEM images. It is found that the distribution is quite narrow, and the mean Pt particle sizes are about 1.5-2.4 nm (Table 1), with the 5Pt/BN having slightly larger Pt size than the other ones. The Pt dispersions (Table 1) based on  $H_2$  chemisorption are



Figure 2. TEM images of (a) 0.2Pt/BN, (b) 0.5Pt/BN, (c) 0.5Pt/BN-H, (d) 1Pt/BN, (e) 2Pt/BN, and (f) 5Pt/BN catalysts.

45-50% except for the SPt/BN sample (33.4%), which are generally consistent with the HRTEM results.

The reduction behavior of the Pt/BN catalysts were measured by  $H_2$ -TPR technique and the profiles are shown in Figure 3. The BN support gives no reduction in the



Figure 3. H<sub>2</sub>-TPR profiles of Pt/BN catalysts with different Pt contents.

employed temperature range. The 0.2Pt/BN, 0.5Pt/BN, and 1Pt/BN catalysts show reduction peaks centered at ca. 100 °C, assigning to the reduction of oxidized Pt species  $(Pt^{n+})$  to metallic Pt (Pt<sup>0</sup>). For the 2Pt/BN and 5Pt/BN catalysts, an additional overlapped reduction peak at ca. 65 °C appears, which means that there are other Pt species in the two catalysts. According to the HRTEM images (Figure 2), it could be concluded that the peak at 100 °C might to due to the reduction of PtO, located at the BN grain boundary, while that at 65 °C is due to the reduction of PtO<sub>x</sub> located on the BN surface. This point is further confirmed by the comparison of the profiles of the 0.5Pt/BN and 0.5Pt/BN-H catalysts, as the 0.5Pt/BN-H has a single reduction peak at 65 °C and it contains randomly dispersed Pt particles on the BN surface. Moreover, the higher reduction temperature implies that the  $PtO_x$ -boundary interaction is stronger than that of the  $PtO_x$ surface interaction, which is in good agreement with the findings in literature.  $^{41,47,49,50}$  Also, the H<sub>2</sub> consumption gradually increases with increasing Pt content in the catalyst, ranging from 6  $\mu$ mol g<sup>-1</sup> for the 0.2Pt/BN to 186  $\mu$ mol g<sup>-1</sup> for the 5Pt/BN.

The oxidation states of the Pt species in the catalysts were determined by XPS, and the results are shown in Figure 4. For the fresh catalysts (Figure 4a), the components at binding energies BEs of 72.8 and 76.2 eV are ascribed to Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  spin—orbital peaks for Pt<sup>2+</sup> species, respectively;<sup>51,52</sup> while the BEs at 74.8 and 77.9 eV are ascribed to Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  spin—orbital peaks for Pt<sup>4+</sup> species, respectively.<sup>53,54</sup> These results suggest that the Pt species exist dominantly in oxidized forms in the calcined catalysts. The relative concentrations of the surface Pt species are summarized in Table 2. It shows that the Pt<sup>2+</sup> and Pt<sup>4+</sup> species in the catalysts are almost equal (about 50%), which is independent of the Pt contents in the catalyst. The species of metallic Pt species at BE of 71.6 eV, suggesting some oxidized Pt species could be reduced by propane during



Figure 4. XPS spectra of Pt 4f of Pt/BN catalysts with different Pt contents.

Table 2. XPS Analyses of Surface Concentrations of Different Pt Species in the Fresh and Spent Catalysts

	relative concentration / %						
		fresh catalyst			spent catalyst		
catalyst	Pt <sup>0</sup>	Pt <sup>2+</sup>	Pt <sup>4+</sup>	Pt <sup>0</sup>	Pt <sup>2+</sup>	Pt <sup>4+</sup>	
0.2Pt/BN	0	49.7	50.3	87.5	12.5	0	
0.5Pt/BN	0	49.0	51.0	73.5	16.3	10.2	
1Pt/BN	0	52.3	47.7	60.6	25.3	14.1	
2Pt/BN	0	54.0	46.0	42.6	43.4	14.0	
5Pt/BN	0	52.0	48.0	41.1	33.0	25.9	
0.5Pt/BN-H	0	41.8	58.2	51.3	28.9	19.8	

the reaction process. The reduction of  $PtO_x$  species by propane might involve the breakage of the C–H bond in propane by either heterolytic or homolytic splitting, which has been regarded as the key steps in alkane oxidation,<sup>55</sup> and thus, the dissociated H species (proton or radical) could react with lattice oxygen to reduce the oxidized Pt. The analyses (Table 2) indicate that the concentration of surface metallic Pt species gradually declines with increasing Pt content. The spent 0.2Pt/ BN has a Pt<sup>0</sup> concentration of 87.5%, while the spent 5Pt/BN has a value of only 41.1%. It is also found that the spent 0.5Pt/ BN has much higher Pt<sup>0</sup> concentration (73.5%) than the spent 0.5Pt/BN-H (51.3%). Considering the morphologies of the catalysts (TEM, Figure 2), it can be deduced that the Pt oxides located on the BN grain boundary could be more easily reduced than those on the surface during the reaction.

3.2. Catalytic Behaviors of the Pt/BN Catalysts. Figure 5a shows the light-off curves of the Pt/BN catalysts for propane combustion. The BN support is inactive in the reaction temperature range. The activity increases with Pt content in the catalyst, while at relative high Pt contents (i.e., 2 and 5 wt %), the catalysts give very close propane conversions. The best performance is obtained on the 5Pt/BN catalyst, with a  $T_{50}$  (reaction temperature at which the propane conversion is 50%) of about 220 °C. Note that the Pt contents in the catalysts are different, specific reaction rates based on Pt contents were calculated at the temperature of 220 °C in the kinetic region (with propane conversion level lower than 10%, detailed results are listed in Table S1) and summarized in Table 1. The specific reaction rates are 92.3, 61.9, 60.5, 44.6, and 19.2  $\mu$ mol  $g_{Pt}^{-1}$  s<sup>-1</sup> for the 0.2Pt/BN, 0.5Pt/BN, 1Pt/BN, 2Pt/BN, and 5Pt/BN catalysts, respectively. These values are higher than many results reported in the literature, and they



Figure 5. (a) Catalytic performance of various Pt/BN catalysts and (b) stability of 2Pt/BN catalyst in reaction conditions with and without H<sub>2</sub>O.



Figure 6. (a) Catalytic behaviors of calcined and prereduced 2Pt/BN catalysts at initial stage. (b) Light-off curves of calcined and prereduced 2Pt/BN catalyst at S.V. of 80 000 mL  $g^{-1}$   $h^{-1}$ .

are comparable to the best results. For example, at reaction temperature of 220 °C, the 15.2Pt/SrTiO<sub>3</sub> gave a rate of 5.46  $\mu$ mol  $g_{Pt}^{-1}$  s<sup>-1</sup>,<sup>38</sup> the 1Pt/Ce<sub>0.33</sub>Zr<sub>0.67</sub>O<sub>2</sub> catalyst gave a rate of 5.46  $\mu$ mol  $g_{Pt}^{-1}$  s<sup>-1</sup>,<sup>36</sup> the 1Pt/Ce<sub>0.33</sub>Zr<sub>0.67</sub>O<sub>2</sub> catalyst gave a rate of 2.98  $\mu$ mol  $g_{Pt}^{-1}$  s<sup>-1</sup>,<sup>56</sup> the 1Pt/1.43Fe/Al<sub>2</sub>O<sub>3</sub> gave a rate of 5.20  $\mu$ mol  $g_{Pt}^{-1}$  s<sup>-1</sup>,<sup>57</sup> the 1Pt/USY catalyst gave a rate of 96.4  $\mu$ mol  $g_{Pt}^{-1}$  s<sup>-1</sup>,<sup>58</sup> and the 1Pt/WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst gave a rate of 80.3  $\mu$ mol  $g_{Pt}^{-1}$  s<sup>-1</sup>,<sup>59</sup> Detailed comparison of the catalytic performance of the Pt catalysts are summarized in Table S2. To compare the intrinsic activity, kinetic-controlled turnover frequencies (TOFs) at 220 °C were calculated on the basis of the Pt dispersions (detailed results were summarized in Table S1). The results in Table 1 show that the 0.2Pt/BN gives the highest TOF of  $36.8 \times 10^{-3} \text{ s}^{-1}$ , whereas the 5Pt/BN give the lowest TOF of  $12.7 \times 10^{-3} \text{ s}^{-1}$ . The 2Pt/BN catalyst was selected for the stability test. As shown in Figure 5b, the catalyst is stable during 50 h reaction (with a propane conversion of about 90%). Moreover, the stability could be sustained under the moisture-containing conditions. The introduction of 2.5% of water vapor in the feed stream even slightly enhances the activity, which makes the catalyst potential in practical application. Also, the HRTEM image of

the spent catalyst (Figure S1b) shows no obvious changes in the size and location of the Pt particles, suggesting the Pt particles are stable under reaction conditions.

3.3. Reconstruction of Surface Pt Species during the **Reaction.** During the catalytic test, an induction period was detected. Figure 6a illustrates the catalytic behavior of the fresh 2Pt/BN catalyst during the first 35 min reaction. A low S.V.  $(10\ 000\ mL\ g^{-1}\ h^{-1})$  was employed in order to strengthen the induction effect. The propane conversion at 1 min reaction is 49.0%, while it gradually increases to 82.6% in 15 min and reaches a steady state afterward. Such induction period implies the possible reconstruction of the catalyst surface or the generation of active sites, which is induced by the participation of the reactants. For comparison, the prereduced 2Pt/BN catalyst shows no obvious induction period, with the constant propane conversion of 95.1% at 250 °C. Also, the steady-state activity of the prereduced 2Pt/BN is higher than that of the calcined one, as well as its light-off activity (Figure 6b). The XPS analysis (Figure 7) of the calcined 2Pt/BN catalyst after reaction (after 30 min reaction at 250 °C) shows that compared to the fresh one, its Pt 4f spectrum contains large



Figure 7. XPS spectra of Pt 4f of calcined and prereduced 2Pt/BN catalyst before and after reaction at 250  $^\circ C$  for 30 min.

portion of metallic Pt<sup>0</sup> (42.6%), accompanied by significant decline in relative concentration of  $Pt^{4+}$  (from 46.0% to 14.0%) and  $Pt^{2+}$  (from 54.0% to 43.4%), suggesting that the Pt oxide could be reduced by the reactant (e.g., propane) during the reaction. The reduction of Pt oxide by the reactant is also confirmed on other catalysts with different Pt loadings (Figure 4). In contrast, the prereduced 2Pt/BN catalyst before reaction contains 70.3% of Pt<sup>0</sup> and 29.7% of Pt<sup>2+</sup> while the relative concentration of Pt<sup>0</sup> slightly decreases to 68.7%. It should be noted that the presence of Pt<sup>2+</sup> species in the reduced catalyst could also be due to the adsorbed surface atoms on Pt surface but not necessarily to the fully oxidized PtO. Nevertheless, the improved activity on the calcined 2Pt/BN during the induction period is likely due to the generation of metallic Pt species on the surface. Besides, it seems that higher concentration of metallic Pt species in the catalyst is beneficial to the higher activity, as the prereduced 2Pt/BN has a higher surface Pt<sup>0</sup> concentration than the calcined one (68.7% versus 42.6%, Figure 7).

3.4. Roles of BN Support in the Reaction. The mechanisms of propane combustion over supported Pt catalysts have been extensively investigated in literature, and it is generally agreed that under high O2/propane ratio, the activation and cleavage of the C-H in propane molecule is the rate-determining step (RDS).<sup>55,60,61</sup> It is also realized that the oxidation states of the Pt species play crucial roles in determining the observed catalytic performance. However, whether metallic or oxidized Pt species are the active sites for the reaction are still in debate. Many previous works suggest that metallic Pt species are the active sites for propane combustion, based on the correlation between Pt oxidation states and the catalytic behaviors.<sup>36,62-65</sup> For example, Yoshida and co-workers concluded that the electrophilic/electrophobic properties of the support is crucial for the oxidation-resistance of Pt species under oxidizing reaction conditions and metallic Pt are more active than the oxidized Pt.<sup>36,62,61</sup> O'Brien et al.<sup>60</sup> also found that the slight deactivation of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts during the reaction is due to the formation of PtO species, which suggests that metallic Pt species are the active sites. In the case of Pt/BN catalysts, Lin et al.<sup>41</sup> concluded that the higher activity for benzene combustion on the Pt/h-BN than that on the  $Pt/Al_2O_3$  was due to the metallic Pt species could

supply more active oxygen atoms. On the contrary, Wu et al.<sup>59</sup> investigated propane combustion over the Pt/WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts and concluded that metastable  $Pt^{\delta^+}$  species generated by Pt-WO<sub>x</sub> interaction are active sites for propane combustion, as the  $Pt^{\delta+}$ -WOx interfacial sites provided centers for activation of propane and the cleavage of C-H bond. Alternatively, some works proposed synergistic role of metallic and oxidized Pt species. A very recent work by Luo et al.58 found that the propane oxidation activity of the Pt/USY catalyst was significantly higher than that of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. On the basis of the in situ diffuse reflectance infrared spectroscopic results, the authors proposed the C–H dissociation on metallic Pt particles and decomposition/desorption of products on oxidized Pt species. Similarly, Enterkin et al.38 conducted propane combustion over Pt/SrTiO<sub>3</sub> nanocuboids catalysts and proposed that the stabilization of a Pt/PtO core/shell structure is vital for the high activity.

In the current work, it could be concluded that the metallic Pt species in the catalyst is more active than the oxidized Pt as evidenced by the observation of the induction period (Figure 6a) and the corresponding XPS analyses (Figure 7). Figure 8



Figure 8. Relationship between TOFs at 220  $^{\circ}\text{C}$  and Pt/Pt^{n+} ratios for various catalysts.

shows the correlation of TOF values at 220 °C and surface Pt<sup>0</sup> concentrations in the catalysts (data taken from Tables 1 and 2). It is found that the TOF value continuously declines with increasing Pt content in the catalyst. For the 0.2Pt/BN, 0.5Pt/ BN, 1.0Pt/BN, and 2.0Pt/BN catalysts, TEM images show that the Pt morphologies are similar (small Pt particles located on the boundary of BN support, Figure 2), but their TOFs vary by 2-fold (Table 1). Because it is concluded that the C-H bond cleavage on the metallic Pt surface is the kinetic-relevant step in alkane combustion and the subsequent oxidation of the intermediate (with the lattice oxygen on the Pt oxide) is fast,<sup>55,60,61</sup> then the metallic Pt species are the active sites; thus, the different TOFs based on total surface Pt atoms (including metallic and oxidized forms) is due to the different Pt<sup>0</sup> surface concentrations in the catalysts. Indeed, it is found that the TOFs monotonically decrease with declining surface Pt<sup>0</sup> concentration. We further normalize the TOF with surface  $\text{Pt}^0$  concentration (TOF\_{\text{Pt}}{}^0, which is defined as TOF divided by surface Pt<sup>0</sup> concentration in Table 2), and the values are relatively constant at Pt contents of 0.2 to 2 wt % (0.033-0.045 s<sup>-1</sup> at 220 °C, Figure 8), which vindicate the proposition that the metallic Pt<sup>0</sup> species are the active sites. It is worthwhile to revisit the unique property of the h-BN support, especially the grain boundary. Generally, the Pt particles supported on conventional oxides such as Al<sub>2</sub>O<sub>3</sub> remains in oxidized form, particularly when the Pt particle size is small and oxidizing atmosphere is presented, <sup>36,62,61</sup> which leads to the loss of activity for propane combustion.<sup>60</sup> However, the results in the current work reveal that the Pt particles on the h-BN are rather small (ca. 2 nm, Table 1 and Figure 2) and the oxidized Pt could be partially reduced in the reaction by propane even excessive oxygen is presented in the feed gas (Table 2). Moreover, the catalyst with lower Pt content shows higher surface Pt<sup>0</sup> concentration (Table 2). Combined with the locations of Pt particles on the support (Figure 2), therefore, it is reasonable to conclude that one role of the grain boundary of h-BN support could stabilize the Pt particles in metallic form probably due to the Pt-BN interaction, as evidenced by the  $H_2$ -TPR results (Figure 3).

On the other hand, however, the fact that the  $TOF_{Pt}^{0}$  values on the 5Pt/BN and 0.5Pt/BN-H catalysts (ca. 0.026 s<sup>-1</sup> at 220 °C) are lower than those on the other catalysts should not be neglected. It implicates that the activity somehow depends on the locations of the Pt<sup>0</sup> species on the BN support as the Pt particles of the 5Pt/BN and 0.5Pt/BN-H catalysts are mainly at the surface while those in the other catalysts are mainly at the grain boundary. To clarify this speculation, kinetics were conducted on the representative 0.5Pt/BN and 0.5Pt/BN-H catalysts. Based on the data in Table S3–S5, some kinetic parameters could be derived, and the results are summarized in Table 3 and Figure 9. For the 0.5Pt/BN catalyst, the power law

Table 3. Kinetic Results of 0.5Pt/BN and 0.5Pt/BN-H Catalysts

$r = k_{app} \left[ C_3 H_8 \right]^a \left[ O_2 \right]^b$						
catalyst	$\stackrel{k_{\rm app}}{/\times10^{-7}}$	а	Ь	$E_{\rm a}$ / kJ mol <sup>-1</sup>		
0.5Pt/BN	5.11	$0.56 \pm 0.02$	$0.31 \pm 0.01$	111.6 ± 8.0		
0.5Pt/BN-H	4.86	$0.81\pm0.01$	$0.42\pm0.03$	172.4 ± 16.5		

rate expression is  $r = 5.11 \times 10^{-7} [C_3H_8]^{0.56} [O_2]^{0.31}$ , while the rate expression for the 0.5Pt/BN-H is 4.86 × 10<sup>-7</sup>  $[C_3H_8]^{0.81} [O_2]^{0.42}$ . First of all, the apparent rate constant on the 0.5Pt/BN is higher than that on the 0.5Pt/BN-H, suggesting the former catalyst is more active than the latter which is consistent with the observed catalytic behaviors

(Figure 5a). Second, the obtained reaction orders with respect to propane and oxygen on both catalysts are different from the results reported in literature. Avila et al.<sup>12</sup> and Garetto et al.<sup>61</sup> reported that at high  $O_2/C_3H_8$  ratio (>10), the reaction order of propane is close to 1 and the reaction order of oxygen is zero or negative (-0.2 to -1.0) over various supported Pt catalysts (i.e., Pt/CeO<sub>2</sub>, Pt/TiO<sub>2</sub>, Pt/MgO, Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/KL, Pt/HY, Pt/ZSM-5, and Pt/Beta). The discrepancy may lie in the different natures of the Pt species in the employed catalysts and those in the current work. In an early review by Burch and Hayes,<sup>55</sup> it was pointed out that the kinetically relevant C-H bond cleavage of the alkane molecule takes place on the metallic Pt surface, which could further react with adsorbed oxygen on Pt (a Pt oxide). This conclusion explains well the observed reaction orders of propane and oxygen on the mentioned catalysts. For example, the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst contains mostly Pt oxides under oxidizing reaction conditions  $(C_3H_8 + O_2)$ <sup>36</sup> which results in difficult adsorption of propane and thus high reaction order of propane (i.e., reaction order of 1); on the contrary, the saturated oxygen on the Pt oxide results in a very low reaction order of oxygen (i.e., reaction order of zero). The 0.5Pt/BN and 0.5Pt/BN-H catalysts employed in the current work contain large content of metallic Pt<sup>0</sup> (Figure 4b and Table 2), which could provide centers for the propane adsorption. Assuming the propane combustion follows a typical Langmuir-Hinshelwood mechanism, the lower reaction order on the 0.5Pt/BN ( $0.56 \pm 0.02$ ) than that on the 0.5Pt/BN-H (0.81  $\pm$  0.01) implies higher surface coverage of propane on the former catalyst, which is probably due to its higher content of metallic Pt<sup>0</sup> species (73.5% versus 51.3%, Table 2). Meanwhile, the presence of metallic Pt species may also account for the positive reaction orders of oxygen, although the values are relatively low (0.3-0.4)because of the copresence of Pt oxide. One interesting observation is that the reaction order of oxygen on the 0.5Pt/ BN (0.31) is lower than that on the 0.5Pt/BN-H (0.42), which is inconsistent with the assumption that the coverage of oxygen should have been lower on the Pt surface containing more metallic Pt atoms. This observation brings up a speculation that oxygen molecules could also adsorb on the BN boundary, which could possibly participate in the reaction. Grant et al. proposed that the BN boundary is capable of generating a peroxygen specie (>B-O-O-N< ), $^{44}$  which are very effective in selective oxidative dehydrogenation of propane to propylene.



Figure 9. Dependence of reaction rate on partial pressure of (a) propane and (b) oxygen and (c) Arrhenius plots of 0.5Pt/BN and 0.5Pt/BN-H catalysts.



Figure 10. Schematic demonstration of the roles of BN support in the reaction.

Such speculation is further justified by the comparison of the apparent activation energies of the two catalysts. As shown in Figure 9c, the Arrhenius plots reveal that the apparent activation energy  $(E_a)$  on the 0.5Pt/BN catalyst is 111.6  $\pm$ 6.2 kJ mol<sup>-1</sup>, which is much lower than that on the 0.5Pt/BN-H (172.4  $\pm$  16.5 kJ mol<sup>-1</sup>). Such comparison is a strong hint that the reaction route on the 0.5Pt/BN catalyst is different than that on the 0.5Pt/BN-H and the grain boundary of the BN support may participate in the reaction. Unfortunately, there is no concrete evidence at the current stage, and more detailed work is required. The TOF and  $TOF_{Pt}^{0}$  of the 0.5Pt/ BN at 210 °C are calculated to be 0.0205 and 0.0280 s<sup>-1</sup>, respectively (based on data in Table S3 and Table 2), which are much higher than those on the 0.5Pt/BN-H catalyst (TOF = 0.0062 s<sup>-1</sup> and TOF<sub>Pt</sub><sup>0</sup> = 0.012 s<sup>-1</sup>). This comparison again highlights the important role of the BN grain boundary.

Nevertheless, the unique properties of the h-BN support allow us synthesize Pt catalysts which are highly active for propane combustion. The metallic Pt species formed during the reaction are considered to be the active sites for this reaction. Moreover, the BN support plays very important roles in the reaction, which is due to its capability to stabilize metallic  $Pt^0$  species at the grain boundary region and its possible involvement in the reaction. Figure 10 demonstrates the in situ reduction of  $PtO_x$  by propane and different intrinsic activities of Pt species on the surface and boundary of the support.

Although Pt/BN catalysts have been reported in the literature, <sup>39,41,48</sup> we would like to highlight the new findings in this work. First of all, the reconstruction of Pt species in the presence of reactants has been revealed, which is responsible for the observed induction period during the reaction process. Moreover, such reconstruction is related to the surface properties of the BN support. The Pt species on the BN boundary could be easily reduced compared with those on the surface, reflecting the role of the support. Second, quantitative comparison based on kinetic investigations well explain the intrinsic differences between the Pt species on the boundary and surface of the BN support. We believe that these findings may provide some useful insight on the better understanding of the uniqueness of the BN material and their potential in catalysis.

#### 4. CONCLUSIONS

In summary, this work reports highly active Pt/BN catalysts for propane combustion, and the catalytic behaviors are closely related to the surface properties of the Pt species. The Pt species could be stabilized at the h-BN grain boundary especially at low loadings. The Pt oxides in the calcined catalysts could be partially reduced to metallic Pt species, and the Pt surface is reconstructed, which is responsible for the enhanced activity. It is found that the metallic Pt species are more active than the oxides, which could lead to the conclusion that the metallic Pt species are the active sites for the reaction. Also, the grain boundary of the BN support could stabilize the metallic Pt species, and it could possibly be involved in the reaction, which effectively explains the higher TOFs on these particles than those on the BN surface.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b03666.

Calculations of Weisz–Prater criterion  $(C_{WP})$  for internal diffusion limitation and Mears' criterion  $(C_M)$ for external diffusion limitation; calculation of Mears' criterion for heat transfer limitation; results for TOF calculation in kinetic region; comparison of the catalytic performance of supported Pt catalysts; reaction rates on 0.5Pt/BN and 0.5Pt/BN-H catalysts for activation energy calculation; dependence of reaction rate on partial pressures of propane and oxygen over 0.5Pt/BN catalyst; dependence of reaction rate on partial pressures of propane and oxygen over 0.5Pt/BN-H catalyst; and TEM images of resh and spent 2Pt/BN catalyst (PDF)

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#### Notes

1479

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