



Deep oxidation of propane over WO_3 - promoted Pt/BN catalysts: The critical role of Pt - WO_3 interface

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ARTICLE INFO

Keywords:

Deep oxidation
Pt catalysts
 WO_3 promotion
Interfacial sites
Reaction mechanism

ABSTRACT

The addition of WO_3 in the Pt/BN catalyst significantly promotes the performance for deep oxidation of propane. A catalyst with a W content of 7 wt.% (1 Pt-7 W/BN) has the highest activity (a reaction rate of $367.1 \mu\text{mol g}_{\text{Pt}}^{-1} \text{s}^{-1}$ at 220°C), which is 7-fold as high as that on the 1 Pt/BN (a reaction rate of $52.4 \mu\text{mol g}_{\text{Pt}}^{-1} \text{s}^{-1}$). The W-promoted catalysts are stable under dry and wet reaction conditions, showing promising potential in practical applications. Based on detailed kinetics and in-situ diffuse reflectance infrared spectroscopy results, the Pt- WO_3 interfacial sites serve as new active sites which are responsible for the improved activity. The facile reaction between propane adsorbed on Pt atom and surface hydroxyl groups on adjacent WO_x accelerates the cleavage of the C-H bond, which is the kinetically essential step in this reaction system.

1. Introduction

Light alkanes are one major category of volatile organic compounds (VOCs) pollutants [1,2], and deep oxidation (catalytic combustion) is a promising technology for the abatement of light alkanes [3]. However, the activation of the C-H bond requires a high energy barrier because of its strong bond strength [4–6]. Therefore, the development of highly effective catalyst is of great importance. Noble metals such as Pt, Pd and Ru [7–9] and transitional metal oxides (such as Co, Ni, Fe, Cu and Mn) [10–13] are commonly employed for deep oxidation of light alkanes.

Deep oxidation of propane over Pt catalysts is usually taken as a model reaction [14–17]. Various works in literature revealed that the cleavage of the first C-H bond in the methyl group is the rate-determining step (RDS) over Pt catalysts, and the reaction kinetics are closely related to the oxygen coverage on the Pt surface [18]. However, the nature of the active sites is still in debate. It is generally believed that metallic Pt species are the active sites for the propane combustion [19,20], but some works argued that oxidized Pt species are responsible for the activity [21,22]. In fact, considering the reaction mechanism in typical conditions (high O_2 /propane ratio), the activation of propane requires metallic Pt species while the subsequent oxidation requires oxygen adatoms on Pt (PtO_x) [23], therefore, both metallic and oxidized Pt species seem equally crucial for the reaction [24]. It was also reported that the promotion of transition metal oxides such as WO_x , MoO_x and VO_x in the Pt catalysts [20,25,26] could significantly

improve the performance. One role of such promotion is due to the enhanced catalyst reducibility. For example, the addition of WO_x in a Pt/ Al_2O_3 catalyst resulted in an increasing concentration of surface $\text{Pt}^{\delta+}$ species, which helps the initial activation of C-H bond [26]. Besides, the acidic nature of transitional metal oxides usually leads to improved surface acidity, which is also believed to be beneficial for the adsorption/activation of propane molecules [27,28].

Although considerable progresses have been made on the promotion of Pt catalysts for deep oxidation of propane, the nature of such promotion needs deep investigation in order to gain a better understanding of the catalyst system. For example, the generation of Pt-promoter interface may change the electronic properties of both species, which consequently alter the adsorption behaviors of the reactants. Besides, such interface may also result in the evolution of new active sites, which generate new reaction pathways than on the bare Pt catalyst. To explore these essential aspects, systematic kinetics and spectroscopic investigations are required. In this work, we prepared a series of Pt-W/BN catalysts with different W contents and tested them for propane combustion. The main focus of the work is to investigate the influence of the Pt- WO_x interaction on the properties of both species and consequently the catalytic behaviors, in the absence of the interference of the support as BN is inert for this reaction. It was found that the addition of WO_x significantly improves the catalytic performance. Detailed characterizations reveal that the Pt- WO_x interaction remarkably changes the reducibility and surface acidity of the catalyst, as well as the oxidation

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<https://doi.org/10.1016/j.apcatb.2020.118858>

Received 29 December 2019; Received in revised form 3 March 2020; Accepted 5 March 2020

Available online 14 April 2020

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states of the Pt species, which in turn exert great impact on the observed catalytic behaviors. More importantly, kinetic experiments and in-situ spectroscopic investigations were conducted in order to further illustrate the roles of WO_x species on the reaction mechanism.

2. Experimental

2.1. Catalyst preparation

Several catalysts with fixed Pt nominal contents of 1 wt.% and different W contents were prepared using a co-impregnation method. Taking the catalyst with a W content of 7 wt.% as an example, 0.0317 mmol of ammonium tungstate hydrate ($(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot x\text{H}_2\text{O}$) was dissolved in 5 ml of aqueous solution of $\text{Pt}(\text{NO}_3)_2$ (2 mg ml^{-1}). One gram of commercial hexagonal BN support (h-BN, Aladdin, 99.9 %) was impregnated with the mixed solution for 3 h at room temperature. The water was evaporated at 90°C under stirring, followed by drying at 100°C overnight and calcination at 500°C in static air for 4 h. The obtained catalyst was denoted as 1 Pt-7 W/BN. Other catalysts were prepared in a similar manner and were labeled as 1 Pt- x W/BN ($x = 0, 1, 3, 5, 7$ and $10 \text{ wt.}\%$), where x was the nominal weight percentage of W in the catalyst.

2.2. Catalyst characterizations

The specific surface areas of the catalysts were measured by N_2 atmosphere at 77 K on a BK200C physical adsorption analyzer. The catalysts were evacuated at 150°C for 4 h before the measurements. The actual contents of Pt and W elements in the catalysts were determined by inductively coupled plasma - atomic emission spectrometry (ICP-AES, IRIS Intrepid 2). The crystalline structures of the catalysts were determined by powder X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer using $\text{Cu K}\alpha$ radiation, which was operated at 40 kV and 40 mA . The scanning range of 2θ was from 10 to 90° with a step of $0.02^\circ \text{ s}^{-1}$.

The Raman spectra of the catalysts were collected on a Renishaw Invia confocal microprobe under ambient condition (laser power = 3 mW , dwell time = 30 s , number of scans = 100 , resolution = 1 cm^{-1}). The wavelength of the excitation laser was 785 nm . Before the measurement, the sample was heated under an infrared lamp (80°C for 15 min) to remove moisture in the sample. Transmission electron microscopy (TEM) images of the catalysts were obtained using a JEOL JEM-2100 F electron microscope operated at 200 kV . High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on a JEM F200 microscope.

The Pt dispersion in the catalyst was determined by CO chemisorption on a Quantachrome ASIQ Win instrument. 100 mg of the catalyst was loaded in an U-tube reactor and pre-reduced at 300°C in $5\% \text{ H}_2 + 95\% \text{ N}_2$ (30 ml min^{-1}) for 1 h , and then it was purged with pure He (30 ml min^{-1}) for another 1 h . After the sample was cooled to 40°C in pure He, high-purity CO pulses were introduced. The Pt dispersion was calculated on the basis of equation $\text{Pt}/\text{CO} = 1/1$.

The reducibility of the catalysts was determined by hydrogen temperature programmed reduction (H_2 -TPR), which was performed on a self-made reaction apparatus equipped with a thermal conductivity detector (TCD). In a typical run, 40 mg catalyst was placed in a quartz tubular reactor (i.d. = 6 mm) and was pretreated in a flow of $10\% \text{ O}_2 + 90\% \text{ N}_2$ (30 ml min^{-1}) at 300°C for 1 h and then cooled down to 30°C . The catalyst was heated from 30 to 850°C in a flow of $5\% \text{ H}_2 + 95\% \text{ N}_2$ (30 ml min^{-1}) at a ramp of $10^\circ\text{C min}^{-1}$. The H_2 consumption was calibrated by the reduction of CuO powder with a known amount. Surface acidity of the catalyst was measured by ammonia temperature-programmed desorption (NH_3 -TPD). In a typical measurement, 300 mg of the catalyst was loaded in a home-made reactor and pretreated at 300°C for 1 h in a flow of $10 \text{ vol.}\% \text{ O}_2 + 90 \text{ vol.}\% \text{ N}_2$ (30 ml min^{-1}). It was then cooled down to 100°C and exposed in a flow of pure NH_3 (30

ml min^{-1}) for 1 h . After the catalyst was purged by pure N_2 (30 ml min^{-1}) at 100°C for 30 min , it was heated to 600°C at a ramp of $10^\circ\text{C min}^{-1}$. The signal of desorbed NH_3 was recorded by a mass spectroscopy (MS, Hiden, QIC-20) at $m/e = 17$.

X-ray photoelectron spectra (XPS) was collected on an ESCALAB 250Xi system with $\text{Al K}\alpha$ source to detect the surface compositions and oxidation states of the elements. The binding energies (BEs) were calibrated by using B1s (290.5 eV) as the reference. Peak deconvolution was conducted using a XPSPEAK41 software.

In-situ diffuse reflectance infrared spectroscopy (DRIFTS) investigations were performed on a Thermal - Fischer Nicolet iS50 FTIR spectrometer equipped with a MCT detector. Certain amount of the catalyst was loaded in a PIKE DRIFT accessory and was pretreated in $0.2 \text{ vol.}\% \text{ C}_3\text{H}_8 + 2 \text{ vol.}\% \text{ O}_2 + 97.8 \text{ vol.}\% \text{ N}_2$ (30 ml min^{-1}) at 450°C for 30 min , followed by N_2 purge for another 30 min . Then it was cooled down to 220°C in a N_2 flow (30 ml min^{-1}), and background spectra were recorded. Afterwards, a mixed flow of $0.2 \text{ vol.}\% \text{ C}_3\text{H}_8 + 99.8 \text{ vol.}\% \text{ N}_2$ (30 ml min^{-1}) or $0.2 \text{ vol.}\% \text{ C}_3\text{H}_8 + 2 \text{ vol.}\% \text{ O}_2 + 97.8 \text{ vol.}\% \text{ N}_2$ (30 ml min^{-1}) was introduced. For the CO adsorption on spent catalyst, the catalyst was exposed to $0.2 \text{ vol.}\% \text{ C}_3\text{H}_8 + 2 \text{ vol.}\% \text{ O}_2 + 97.8 \text{ vol.}\% \text{ N}_2$ (30 ml min^{-1}) at 250°C for 2 h , and was cooled down to room temperature in N_2 . Then $5 \text{ vol.}\% \text{ CO}$ in N_2 was introduced for 30 min and purged with N_2 for 30 min .

2.3. Activity test and kinetic investigation

Deep oxidation of propane was performed in a fixed-bed reactor. Fifty milligrams of the catalyst ($60\text{--}80 \text{ mesh}$) diluted with 150 mg of quartz sand with same size was placed in a tubular quartz reactor (i.d. = 6 mm). The feed reaction gas consisted of $0.2\% \text{ C}_3\text{H}_8$, $2\% \text{ O}_2$ and N_2 in balanced with a total flow rate of 67 ml min^{-1} ($\text{GHSV} = 80000 \text{ ml g}_{\text{cat}}^{-1} \text{ h}^{-1}$). Before reaction, the catalyst was aged in the reactant mixture at 480°C for 30 min and cooled down to 450°C . The reaction was then conducted from 450 to 180°C . The concentrations of the outlets gas and products were analyzed online by a gas chromatography (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a capillary column (DB-WAX, $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$). The C_3H_8 conversion ($X_{\text{C}_3\text{H}_8}$) was calculated by the following equation:

where $[\text{C}_3\text{H}_8]_{\text{in}}$ and $[\text{C}_3\text{H}_8]_{\text{out}}$ are the C_3H_8 concentrations in the inlet and outlet gas, respectively. No organic by-products were detected. The catalysts were also tested under moisture-containing reaction conditions, where $2.5 \text{ vol.}\%$ of water vapor was introduced in the feed gas stream by passing the reactant through a bubbler kept at 0°C .

The reaction kinetics over some representative catalysts were performed at differential reaction mode (with propane conversion below 15%). The catalyst was diluted with quartz sand (with same size) to 100 mg , and it was aged under the same condition as in catalytic test. Both the absence of internal and external diffusion was verified, which includes Weisz-Prater criterion (C_{WP}) for internal diffusion, Mears' criterion (C_{M}) for external diffusion and Mears' criterion (C_{M}) for heat transfer (see Supporting Information for detailed calculation). The reaction orders of propane and oxygen were measured at high $\text{O}_2/\text{C}_3\text{H}_8$ ratios, as the propane partial pressures were controlled at $0.202\text{--}0.808 \text{ kPa}$ and those of the oxygen were controlled at $1.515\text{--}9.09 \text{ kPa}$.

3. Results and discussion

3.1. General characterizations

The prepared catalysts have similar surface areas ($19\text{--}24 \text{ m}^2 \text{ g}^{-1}$, Table 1). The actual Pt and W contents in the catalysts are close to the nominal values. The XRD patterns (Fig. 1a) show that all the catalysts give typical diffraction peaks at 2θ of $26.8, 41.6, 43.9, 50.1$ and 55.1° , assigning to hexagonal BN (JCPDS No. 34-0421). No diffractions corresponding to Pt or PtO_x are detected, indicating the Pt species (Pt or PtO_x) are highly dispersed on the surface of support. The addition of W

Table 1
Physical properties and kinetic-controlled activities of various 1 Pt-xW/BN catalysts.

Catalyst	S_{BET} / $\text{m}^2 \text{g}^{-1}$	Content / wt.%		Pt size ^a / nm	CO uptake / $\mu\text{mol g}_{\text{cat}}^{-1}$	D_{Pt} ^b / %	C_3H_8 Conv. ^c / %	Reaction rate ^d / $\mu\text{mol g}_{\text{Pt}}^{-1} \text{s}^{-1}$	TOF ^d / $\times 10^{-3} \text{s}^{-1}$
		Pt	W						
1 Pt/BN	19	0.96	-	2.0 ± 0.5	23.4	47.9	10.1@ 20 mg	52.4 ± 3.7	21.4 ± 1.5
1 Pt-1W/BN	20	0.93	0.97	n.d.	5.7	12.0	13.3@ 15 mg	95.1 ± 6.7	154.4 ± 10.8
1 Pt-3W/BN	22	1.04	2.70	n.d.	5.2	9.8	9.7@ 10 mg	94.3 ± 6.6	187.7 ± 13.1
1 Pt-5W/BN	24	1.10	5.21	n.d.	4.8	8.5	7.7@ 5 mg	141.2 ± 9.9	323.9 ± 22.7
1 Pt-7 W/BN	23	0.99	6.68	3.0 ± 0.5	3.9	7.8	14.6@ 4 mg	367.1 ± 25.7	917.7 ± 64.2
1 Pt-10W/BN	20	0.94	9.82	n.d.	3.7	7.9	12.9@ 5 mg	277.1 ± 19.4	684.0 ± 47.8

^a Determined by TEM.

^b Dispersion of Pt was determined by CO chemisorption.

^c Data were taken after 3 h at reaction temperature of 220 °C and the errors are about 7 %.

^d Reaction rates and TOF values were calculated under kinetic region with propane conversion level less than 15% and Pt dispersion.

in the catalyst results in distinct diffractions of monoclinic WO_3 at 2θ of 23.1, 23.6 and 34.2 ° (JCPDS No. 43-1035). Meanwhile, weak diffraction at 2θ of 39.8° emerges, which could be assigned to metallic Pt (JCPDS No. 04-0802). The Raman spectra of the catalysts (Fig. 1b) give bands at 708 and 805 cm^{-1} with the addition of W, assigning to asymmetric and symmetric stretching vibration of W-O-W bonds in monoclinic WO_3 [29,30]. The spent 1 Pt-7 W/BN catalyst gives almost identical bands as the fresh one, suggesting the structure of the WO_3 species remains stable during the reaction.

Fig. 2 displays the representative HRTEM images of the 1Pt/BN and 1Pt-7W/BN catalysts (Fig. 2a–d). The 1Pt/BN catalyst shows uniform Pt particles with sizes of 2.0 ± 0.5 nm dominantly located on the grain boundary of h-BN support (Fig. 2a, Table 1). The 1Pt-7W/BN catalyst also shows similar location of the Pt particles, with particle sizes of 3.0 ± 0.5 nm (Fig. 2b). The selective deposition of the metal species on the BN boundary has been also observed in Pt/BN and Au/BN catalysts [31,32], because the negatively charged N-rich boundaries could stabilize the Pt^{2+} and W^{6+} cations in the precursors [31,33,34]. Detailed analyses of the morphologies (Fig. 2c and d) reveal the presence of both metallic and oxidized Pt species, as well as the WO_3 species, which is evidenced by the d-space fringe measurements ($\text{Pt}(200) = 0.198$ nm, $\text{PtO}_2(120) = 0.207$ nm, $\text{WO}_3(-301) = 0.233$ nm). Contacting Pt and WO_3 species are also observed (Fig. 2c). Such interaction is further confirmed by the HAADF-STEM-EDS mapping analyses of the 1 Pt-7 W/

BN catalyst (Fig. 2e–h). The relatively homogeneous distribution of the Pt and the WO_x species is likely due to the aqueous impregnation used and the hydrophobic nature of the BN support. But some rather large WO_x particles (up to about 50 nm) are observed due to its high content. In addition, overlapped Pt and W entities are observed. The interaction of the Pt and W species are further confirmed by the CO chemisorption results (Table 1), the CO uptakes drastically decline with the addition of W, therefore the Pt dispersion based on CO chemisorption is much lower than that determined by TEM. For example, the Pt dispersion of the 1 Pt-7 W/BN by CO chemisorption is 7.7 % (corresponding to an average Pt size of 14.8 nm), which is much larger than that by TEM (3.0 nm). This large difference reflects the coverage of surface Pt atoms by WO_x species, which is well consistent with HAADF-STEM results (Fig. 2e–h).

The H_2 -TPR profiles of the catalysts are shown in Fig. 3a. The 1 Pt/BN catalyst only shows a reduction peak centered at around 90 °C attributed to the reduction of PtO_x to Pt [31,34] with a H_2 consumption of $21 \mu\text{mol g}^{-1}$, which corresponds to an average Pt valence of + 0.8. However, this value is likely underestimated because some oxidized Pt species could be readily reduced upon the exposure to H_2 at ambient temperature and thus the signal was not recorded. The 1 Pt-1W/BN catalyst gives two reduction peaks at 100 and 350 °C, which are ascribed to the reduction of PtO_x to metallic Pt and the reduction of WO_3 to $\text{WO}_{2.9}$ [35], respectively. The high temperature reduction peak

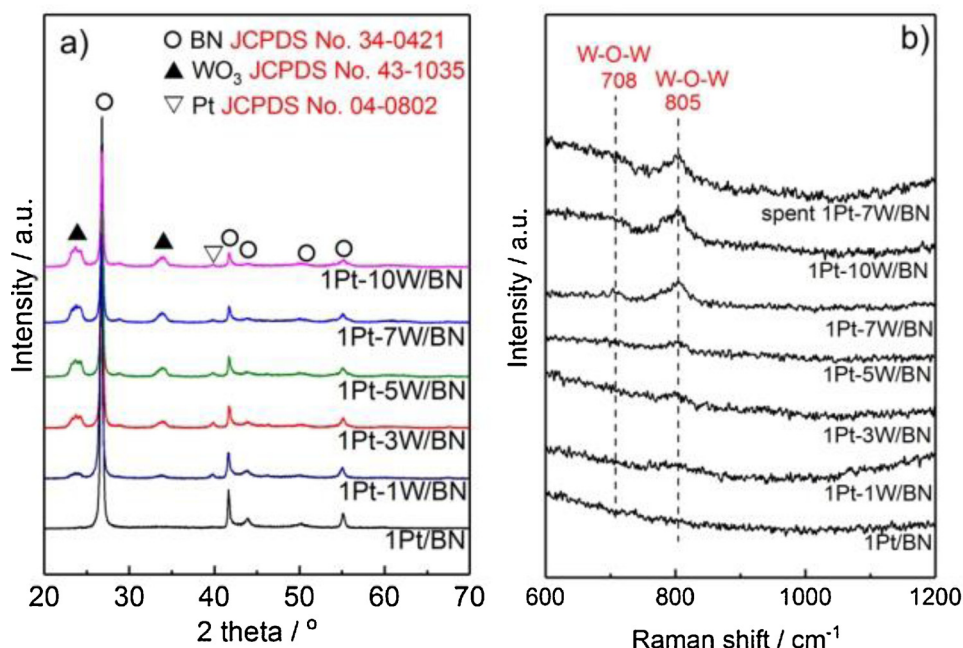


Fig. 1. a) XRD patterns and b) Raman spectra of various 1 Pt-xW/BN catalysts.

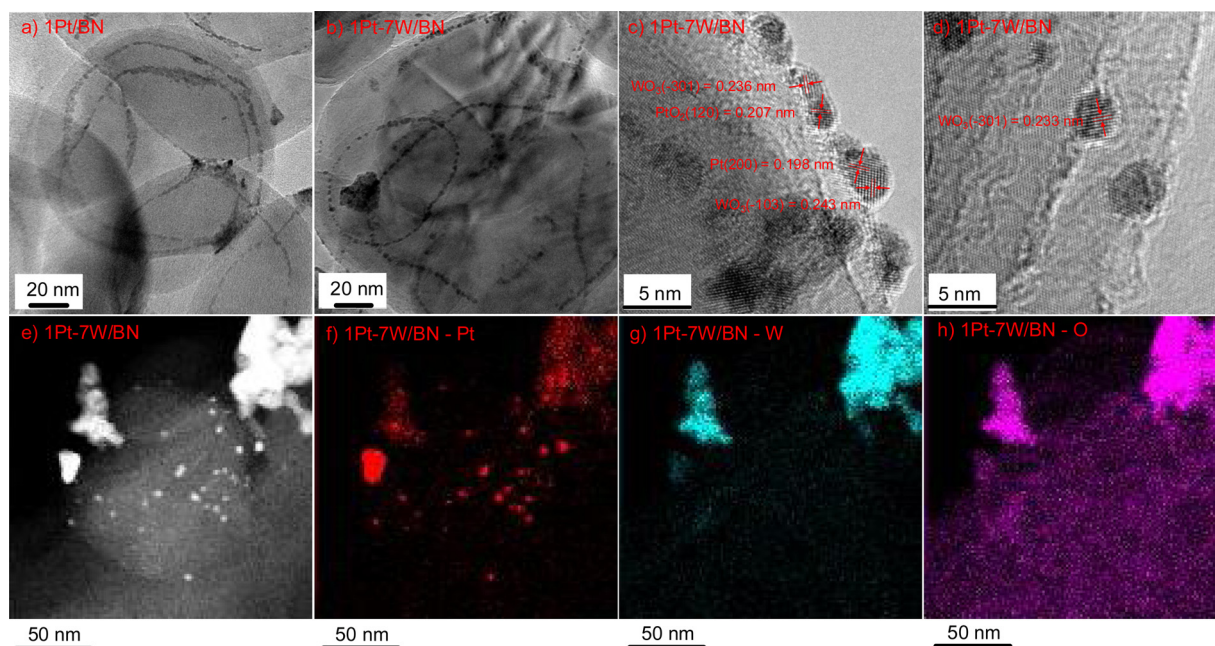


Fig. 2. a)-d) TEM images of 1 Pt/BN and 1 Pt-7 W/BN catalysts; e)-h) HAADF-STEM-EDS mapping analyses of 1 Pt-7 W/BN catalyst.

(> 550 °C) is attributed to the sequential reduction of $WO_{2.9}$ to WO_2 (550 - 700 °C) and WO_2 to W (750 - 850 °C) [36]. The H_2 consumption either in low temperature (LT) or high temperature (HT) region increases with W content in the catalyst, ranging from 24 to 69 $\mu\text{mol g}^{-1}$ and 173 to 926 $\mu\text{mol g}^{-1}$, respectively. Note that the LT H_2 consumption is not proportional to the W content in the catalyst, which reflects different Pt- WO_x interactions or WO_x dispersions in these catalysts. Fig. 3b shows the NH_3 -TPD profiles of the catalysts. The 1 Pt/BN catalyst shows negligible acidity. The addition of W in the 1 Pt/BN catalyst results in desorption peaks in range of 200 - 480 °C, indicating the presence of medium and strong acid sites on these catalysts. The relative surface acidity of the catalysts reaches the maximum at W content of 7 wt.% (5.60). According to literature [37,38], the acid sites could be improved with increasing WO_x loading and reached the maximum at the monolayer coverage (dispersion threshold). The surface monotonungstate species at low WO_x content showed low acidity while the polytungstate became dominant at the monolayer WO_x coverage and possessed strong acid sites due to the generation of

interconnected WO_x species. But further increase in WO_x loading led to the formation of crystalline m- WO_3 phase, which makes no contribution to the total acidity.

Fig. 4 shows the Pt 4f XPS spectra of the fresh and spent catalysts. Since Pt 4f signal overlaps with W 5s signal, the latter was subtracted when fitting the Pt 4f spectra. For the fresh catalysts (Fig. 4a), the Pt 4f_{7/2} spectrum of the fresh 1 Pt/BN catalyst contains two components at BEs of 72.5 and 74.7 eV, assigning to Pt^{2+} and Pt^{4+} species, respectively [39,40]. No obvious peaks of metallic Pt^0 are observed. The result suggests that the Pt species exist dominantly in oxidized forms in the calcined catalysts. The addition of W in the catalyst results in a new component at BE of 71.5 eV assigning to metallic Pt^0 [41,42]. It also should be noted that the intensities of the Pt 4f spectra gradually decline with increasing W content, which may be attributed to the fact that Pt particles are covered by WO_3 , as evidenced by the HAADF-STEM-EDS mapping analyses results (Fig. 2e-f). The analyses of surface Pt/W molar ratio (Table S1) further confirm this proposition, as the Pt/W generally decreases with increasing W content in the catalyst. For the

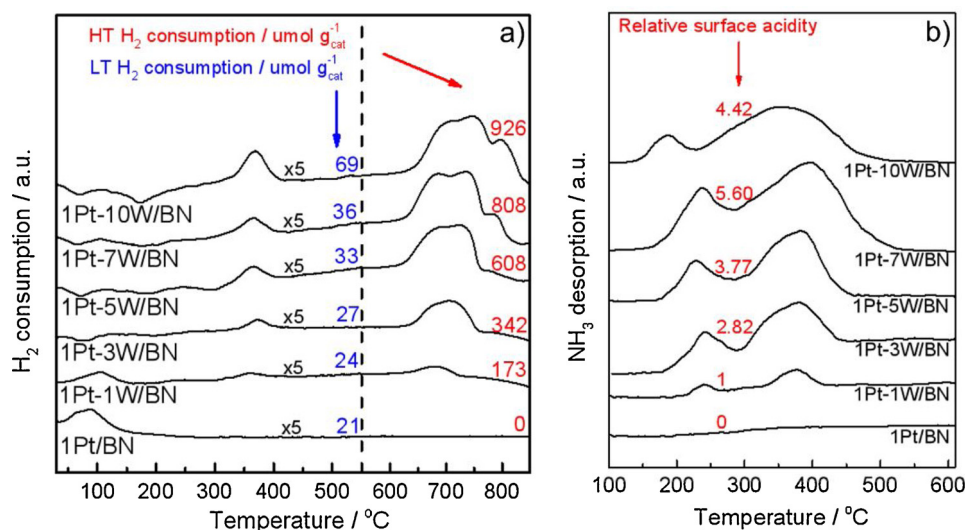


Fig. 3. a) H_2 -TPR profiles and b) NH_3 -TPD profiles of various 1 Pt-xW/BN catalysts.

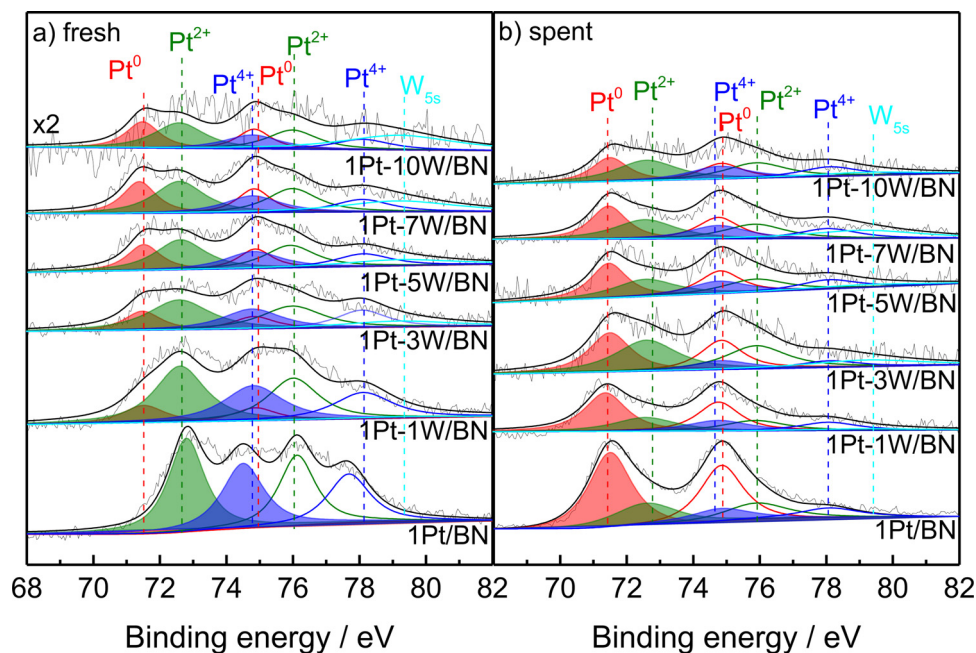


Fig. 4. XPS spectra of Pt 4f of various 1 Pt-xW/BN catalysts.

spent catalysts (Fig. 4b), one distinct difference compared to the corresponding fresh one is that the surface concentration of metallic Pt species is remarkably higher. This is due to the reduction of Pt oxide by propane under the reaction conditions, as reported in our previous work on Pt/BN catalysts with different Pt loadings [19]. Suggesting the partial reduction of Pt oxide during the reaction. However, with the increase of WO_3 content, the concentrations of metallic Pt species in the fresh and spent catalysts become close, as summarized in Table S1. These findings suggest that the presence of WO_x in the catalyst could stabilize the Pt oxides via Pt-W interaction, which is ascribed to electron transfer from W to Pt species leads to a higher electron density around Pt [43]. Also, the surface Pt/W molar ratio in the spent catalysts (Table S1) are similar to those in the fresh ones, suggesting that the catalyst surface remains stable during the reaction process.

The electronic properties of the Pt species in the spent catalysts were further investigated by CO-DRIFTS, as shown in Fig. S1. All the catalysts show a broad band in range of $1800 - 2200 \text{ cm}^{-1}$, which consists of three components at 2042 , 2071 and 2091 cm^{-1} , assigning to CO adsorbed on terrace Pt^0 site, on step Pt^0 site and on oxidized Pt species, respectively [26]. The band intensities of the W-containing catalysts are much lower than that of the 1Pt/BN, suggesting less exposed surface Pt atoms in these catalysts due to the coverage of Pt surface by WO_x species.

3.2. Catalytic behaviors of the catalysts

Fig. 5a shows the performance of the catalysts for deep oxidation of propane. The 7 W/BN is inactive in low temperature region, indicating very limited contribution of the WO_x species and homogeneous gas phase oxidation of propane. The 1Pt/BN shows considerable activity. The addition of WO_x in the catalyst significantly improves the activity and the propane conversion increases with increasing W content up to 7 wt.%, but declines with higher W content (i.e. 10 wt.%). The activities of the catalyst drastically increase when the reaction temperature is higher than 250°C , however, the catalysts also show considerable reactivity at low temperature region. For example, the 1 Pt-7 W/BN catalyst gives a propane conversion of 14.8 % at 180°C . To compare the activities with those reported in literature, the mass specific reaction rates are calculated based on the Pt content in the catalyst ($\mu\text{mol g}_{\text{Pt}}^{-1} \text{ s}^{-1}$), and summarized in Table 1. The highest reaction rate at 220°C is

obtained on the 1 Pt-7 W/BN ($367.1 \mu\text{mol g}_{\text{Pt}}^{-1} \text{ s}^{-1}$). These values are much higher than most of the Pt catalysts reported in literature (Table S1). For example, at reaction temperature of 220°C , the 15.2 Pt/SrTiO₃ gave a rate of $5.46 \mu\text{mol g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ [44], the 1 Pt/Ce_{0.33}Zr_{0.67}O₂ catalyst gave a rate of $2.98 \mu\text{mol g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ [45], the 1 Pt/1.43Fe/Al₂O₃ gave a rate of $5.20 \mu\text{mol g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ [6], the 1 Pt/USY catalyst gave a rate of $96.4 \mu\text{mol g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ [22], and the 1 Pt/ WO_x /Al₂O₃ catalyst gave a rate of $80.3 \mu\text{mol g}_{\text{Pt}}^{-1} \text{ s}^{-1}$ [26]. Moreover, kinetic-controlled turnover frequencies (TOFs) at 220°C were calculated based on Pt dispersions (Table 1). The TOF on the 1 Pt-7 W/BN (0.917 s^{-1}) is 45 times higher than that on the 1 Pt/BN (0.0214 s^{-1}), reflecting the crucial promoting role of WO_x . The representative 1 Pt-7 W/BN catalyst was selected for stability testing. As shown in Fig. 5b, the catalyst is stable during 60 h reaction at 250°C (with a propane conversion of about 95.6 %). Moreover, the stability could be sustained under the moisture-containing conditions. The introduction of 2.5 % of water vapor in the feed stream hardly affects the activity and the catalyst remains stable, which makes it potential in practical application. At reaction temperature of 200°C , the 1 Pt-7 W/BN catalyst remains its stability under dry and wet conditions, however, the presence of moisture somehow leads to a drop of propane conversion of about 6 - 7 % compared to that in the dry condition, probably due to the competitive adsorption of H₂O and CO₂ on the Pt surface particularly at low temperature [46].

For propane combustion over Pt catalysts, the catalytic performance is influenced by multiple factors. It was reported that larger Pt particles are generally more active than the smaller ones in alkane combustion [47] due to the decreased Pt-O bond strength with increasing Pt particle, which leads to more reactive adsorbed oxygen species on Pt sites. It was also reported that the oxidation states (chemical valence) of the Pt species are essential. Many works suggest that metallic Pt species are more active than oxidized Pt species [20,21,24,48]. However, some works drew opposite conclusions that Pt oxides are more active than the metallic Pt. Wu et al. [26] found that the Pt/ WO_x /Al₂O₃ was more active than the Pt/Al₂O₃ because it contained more $\text{Pt}^{\delta+}$ species via Pt- WO_x interaction. Such contradiction reflects complicated factors in determination of the catalytic behaviors, which may also involve different reaction mechanisms related to the nature of the Pt species. With the addition of transition metal oxides in the Pt catalysts as the promoter, the scenario becomes even more tangled because the addition of promoter not only changes the properties of Pt species (i.e. particle size

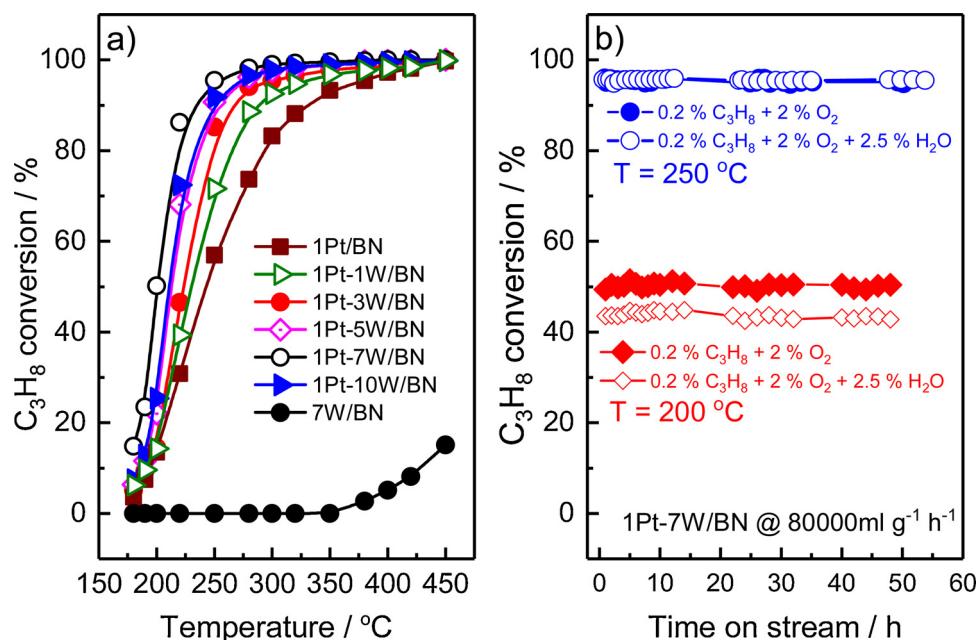


Fig. 5. a) Propane conversions on various catalysts at elevated temperatures, b) Catalyst stability of 1 Pt-7 W/BN catalyst under dry and wet reaction conditions.

and oxidation states) via Pt-promoter interaction but also changes the surface properties (i.e. reducibility and surface acidity) of the catalyst. The importance of reducibility has been well recognized in oxidation reaction as it is related to the activation of the oxygen species; while the surface acid sites provide centers for propane adsorption [22] and/or activation [26].

In the current case, the TEM results (Fig. 2 and Table 1) suggest similar Pt particle distributions in the 1 Pt/BN and 1 Pt-7 W/BN catalysts, which implies that the Pt particle size may not be the main factor in determining the observed catalytic behaviors. Regarding the roles of oxidation states of the Pt species, the XPS results (Fig. 4 and Table S1) reveal that the spent 1 Pt/BN catalyst has the highest surface concentration of metallic Pt (67.4 %, Table S1), yet it gives the lowest activity (Table 1). Thus, it could be safely concluded that the metallic Pt species may not be the main active sites in the current system. Besides, it seems that the behaviors of the catalysts are closely related to their reducibility and surface acidity. The H₂-TPR (Fig. 3a) and NH₃-TPD (Fig. 3b) results show that the H₂ consumption and surface acidity increase with the W content up to 7 wt.%, which coincides with the trend of observed activity, and thus provide strong implication that the roles of WO₃ promotion might be due to the enhanced reducibility and surface acidity of the catalyst.

However, it should be noted that the structure – performance correlation established on these catalysts is not sufficient enough to obtain a thorough understanding the roles of WO₃ promotion. Therefore, kinetic investigation was conducted in order to gain some deep insights on the different behaviors of the catalysts.

3.3. Kinetic investigation

The kinetic experiments were conducted on two representative catalysts, 1 Pt/BN and 1 Pt-7 W/BN. The C₃H₈/O₂ ratios were controlled in range of 1/7.5 - 1/45, in which oxygen are excessive (detailed results are summarized in Table S3 and S4). Fig. 6a shows that the reaction rates increase with increasing partial pressure of propane. However, the reaction rate decreases with increasing partial pressure of oxygen, as shown in Fig. 6b. The derived power law rate expressions are $r = 6.68 \times 10^{-6} [\text{C}_3\text{H}_8]^{1.30} [\text{O}_2]^{-0.67}$ for the 1 Pt/BN, and $r = 27.32 \times 10^{-6} [\text{C}_3\text{H}_8]^{1.29} [\text{O}_2]^{-0.38}$ for the 1 Pt-7 W/BN, and the parameters are summarized in Table 2. A brief discussion of these parameters is

necessary. First, the much higher apparent rate constant k on the 1 Pt-7 W/BN catalyst suggests its higher intrinsic activity than the 1 Pt/BN catalyst, which is in agreement with the observed overall performance (Table 1 and Fig. 5). Second, the reaction orders of propane on both catalysts are about 1. These values are similar to those obtained on other Pt catalysts. Avila et al. [49] conducted kinetic of propane combustion over various Pt catalysts (Pt/TiO₂, Pt/CeO₂ and Pt/Al₂O₃) and found that the reaction orders of propane on these catalysts were 0.8 - 1.5. The high reaction order of propane is probably related to the weak adsorption of propane because of its stable structure, and to its competitive adsorption with O₂ on Pt surface [49]. Third, the negative reaction orders of oxygen on both catalysts suggest the inhibiting role of oxygen species. However, such inhibiting role is less intense on the 1 Pt-7 W/BN catalyst than that on the 1 Pt/BN, as the former catalyst gives a higher reaction order of oxygen (-0.38) compared to the latter one (-0.67). It has been well recognized that in light alkane combustion, the reaction order of O₂ is strongly dependent on the reaction conditions particularly the O₂/C₃H₈ ratio in the feed stream, as it changes the oxygen coverage on the Pt surface atoms [49,50]. For example, detailed kinetics on combustion of methane, ethane and propane over Pt/Al₂O₃ catalysts [18,23] revealed three distinct kinetic regions. The reaction order of O₂ is positive when O₂/C₃H₈ ratio is low (i.e. 1 - 5) because the rate-determining step (RDS) is the activation of oxygen on the metallic Pt surface atoms; The reaction order of O₂ is negative when O₂/C₃H₈ ratio is medium (i.e. 5 - 20) because the RDS is the activation of propane on partially oxygen covered Pt surface (*-O); The reaction order of O₂ is zero when O₂/C₃H₈ ratio is high (i.e. > 20) because the RDS is the activation of propane on fully oxygen covered Pt surface (O *-O). In the current case, the negative reaction orders of oxygen on both catalysts are obtained in O₂/C₃H₈ ratios of 10 - 40 (Tables S3 and S4), and under such condition the Pt surface is partially covered by oxygen as the XPS results (Table S1 and Fig. 4) reveal the presence of metallic and oxidized Pt species in the spent catalysts. Fourth, the apparent activation energies (E_a) of the catalysts (Table 2) are much higher than those on other supported Pt catalysts (i.e. 37–84 kJ mol⁻¹ for Pt/TiO₂, Pt/CeO₂ and Pt/Al₂O₃) [49], probably due to different natures of the supports and reaction conditions. Nevertheless, the E_a of the 1 Pt-7 W/BN (96.1 ± 14.3 kJ mol⁻¹, Fig. 6c, derived on the basis of the data in Table S5) is significantly lower than that of the 1 Pt/BN (149.0 ± 24.6 kJ mol⁻¹), which suggests that the reaction may follow different

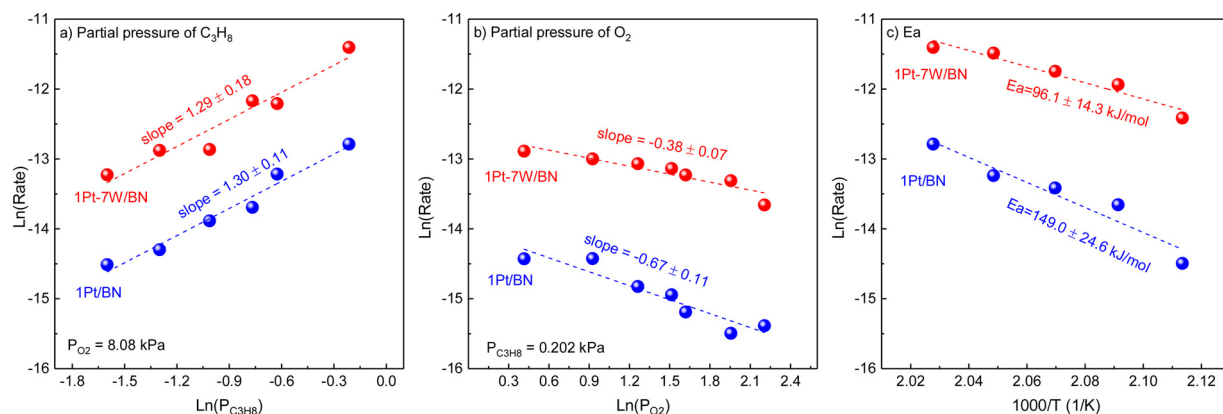


Fig. 6. Dependence of reaction rate on partial pressure of a) propane and b) oxygen and c) Arrhenius plots of 1 Pt/BN and 1 Pt-7 W/BN catalysts.

Table 2

Kinetic results of 1 Pt/BN and 1 Pt-7 W/BN catalysts.

$r = k_{app} [C_3H_8]^a [O_2]^b$				
Catalyst	$k_{app} / \times 10^{-6}$	a	b	Ea / kJ mol ⁻¹
1 Pt/BN	6.68	1.30 ± 0.11	-0.67 ± 0.11	149.0 ± 24.6
1 Pt-7 W/BN	27.32	1.29 ± 0.18	-0.38 ± 0.07	96.1 ± 14.3
$r = kK_{C_3H_8}P_{C_3H_8}/(1 + K_{O_2}P_{O_2} + K_{C_3H_8}P_{C_3H_8})$				
	$k / \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$	$K_{C_3H_8} / \text{ kPa}^{-1}$	$K_{O_2} / \text{ kPa}^{-1}$	
1 Pt/BN	3.0	0.11	2.01	
1 Pt-7 W/BN	16.7	0.12	0.20	

pathways on these two catalysts and new active sites may exist on the 1 Pt-7 W/BN catalyst. Finally, the parity plot and residual analyses of the data (Fig. S2) vindicate the validity of the kinetic results.

The kinetics on the 1 Pt/BN catalyst are similar to those on Pt/Al₂O₃ catalysts for total oxidation of light alkanes (methane and ethane) [23]. Particularly, the negative reaction order of oxygen is a strong implication that the RDS is the activation of propane on partially oxygen covered Pt surface (*-O) [18], which has also been well recognized in catalytic combustion of light alkanes over Pt catalysts [23,51,52]. Therefore, elementary steps on the 1 Pt/BN catalyst could be proposed, which are similar to those proposed by García-Diéguez et al. for methane and ethane oxidation over Pt/Al₂O₃ catalysts [23]. As shown in Table 3, the catalytic cycle mainly includes: 1, Dissociative adsorption of oxygen on Pt surface atom (eqs. 1 and 2); Adsorption of propane on Pt surface atom (eq. 3); 3, Reaction between adjacent adsorbed oxygen and propane to break the first C-H bond in propane (eq. 4), which is the RDS step [18]. The sequential oxidation of the intermediate requires nine oxygen atoms to form the final products (CO₂ and H₂O), which is very fast [53]; Desorption of CO₂ and H₂O from Pt surface atoms (eqs. 5 and 6).

Table 3

Proposed elementary steps on 1 Pt/BN and 1 Pt-7 W/BN catalysts.

$O_2 + * \xrightarrow{K_{O_2}} O_2^*$	(eq. 1)
$O_2^* + * \rightarrow 2O^*$	(eq. 2)
$C_3H_8 + * \xrightarrow{K_{C_3H_8}} C_3H_8^*$	(eq. 3)
$C_3H_8^* + O^* \xrightarrow{k} C_3H_7^* - OH^* (RDS) \xrightarrow{+9O^*} CO_2^* + H_2O^*$	(eq. 4)
$C_3H_8^* + WO_3 \xrightarrow{k_1} C_3H_7^* - WO_2 - OH (RDS) \xrightarrow{+9O^*} CO_2^* + H_2O^*$	(eq. 4')
$CO_2^* \rightarrow CO_2 + *$	(eq. 5)
$H_2O^* \rightarrow H_2O + *$	(eq. 6)
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$	Overall reaction

*Refers to vacant Pt surface sites.

Thus, the rate expression could be derived as follows, assuming the adsorbed oxygen species are the most abundant surface intermediate (MASI)

$$r = kK_{C_3H_8}P_{C_3H_8}/(1 + K_{C_3H_8}P_{C_3H_8} + K_{O_2}P_{O_2})$$

This rate expression implies that the inhibiting role of oxygen in the reaction is due to its competitive adsorption with propane on the surface Pt atoms. According to the high reaction order of propane (very low adsorption equilibrium of propane, $K_{C_3H_8}$), this rate expression could be simplified to $r = kK_{C_3H_8}P_{C_3H_8}/(1 + K_{O_2}P_{O_2})$, which gives a unity reaction order of propane and a negative reaction order of oxygen.

For the 1 Pt-7 W/BN catalyst, although the kinetics are similar to those on the 1 Pt/BN, the much lower Ea (96.1 ± 14.3 kJ mol⁻¹) compared to that on the 1 Pt/BN (149.0 ± 24.6 kJ mol⁻¹) strongly implies the presence of different active sites in the W-containing catalyst, which possess higher activity than the Pt sites. Similar additional active sites were also proposed on Pt/CeO₂ catalyst for propane combustion. Avila et al. [49] found that the Ea on the Pt/CeO₂ catalyst (37 kJ mol⁻¹) was much lower than that on the Pt/Al₂O₃ (60 kJ mol⁻¹) and they proposed Pt⁰-Ce³⁺ interfacial sites in the former catalyst in addition to Pt⁰-Ptⁿ⁺ sites. In the current case, the 7 W/BN is inactive and the 1 Pt/BN is much less active at 220 °C, the new active sites are most likely located at Pt-WO_x interface. On such Pt-WO_x interfacial sites, the propane adsorbed on metallic Pt surface atoms could facilitate react with the active oxygen species on WO_x (either adsorbed oxygen or lattice oxygen in WO₃ or surface hydroxyl groups) to break the C-H bond (RDS), which could be further oxidized to CO₂ and H₂O, as shown in eq. 4'. Indeed, such Pt-WO_x interfacial sites were also proposed by Wu et al. [26], as the authors attributed the enhanced activity of propane combustion over the WO₃-promoted Pt/WO_x/Al₂O₃ than over the Pt/Al₂O₃ to the generation of Pt-WO_x interface.

The derived rate expression according to eq. 4' is similar to that on the 1 Pt/BN, which is

$$r = k_1K_{C_3H_8}P_{C_3H_8}/(1 + K_{C_3H_8}P_{C_3H_8} + K_{O_2}P_{O_2})$$

Therefore, the reaction on the 1 Pt-7 W/BN catalysts follow two different pathways, which take place on Pt⁰-Ptⁿ⁺ pairs and Pt⁰-WO_x interfacial sites. The combination of the rate expressions on the two sites lead to

$$r = k'K_{C_3H_8}P_{C_3H_8}/(1 + K_{C_3H_8}P_{C_3H_8} + K_{O_2}P_{O_2}), \text{ where } k' = k + k_1.$$

Unfortunately, the proportions of the Pt⁰-Ptⁿ⁺ pairs and Pt⁰-WO_x interfacial sites in the 1Pt-7W/BN catalyst could not be successfully quantified. Nevertheless, the kinetic parameters (rate constant of the RDS, k ; adsorption equilibrium constants of propane ($K_{C_3H_8}$) and oxygen (K_{O_2}) could be derived by nonlinear data regression. As shown in Table 2, the 1Pt/BN gives a much lower rate constant k ($3.0 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$) than the 1Pt-7W/BN ($16.7 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$), which highlights the significant contribution of the Pt-WO_x interfacial sites in

the reaction. The adsorption equilibrium constants of propane on both catalysts are low ($0.11\text{--}0.12\text{ kPa}^{-1}$), indicating weak adsorption of propane on the catalysts. It was reported that the surface acid sites are beneficial to the adsorption of propane [22,47,54]. However, the low and similar adsorption equilibria of propane on both 1Pt/BN and 1Pt-7W/BN ($0.11\text{--}0.12\text{ kPa}^{-1}$) suggest that the surface acidity does not play significantly role in the reaction (at least in the current work) although the latter has higher surface acidity than the former. Considering the adsorption equilibrium of oxygen, it is found that the 1Pt/BN gives a much higher value (2.01 kPa^{-1}) than the 1Pt-7W/BN (0.20 kPa^{-1}), suggesting the higher oxygen coverage on the former catalyst. This is because the 1Pt/BN contain higher concentration of surface metallic Pt species (60.6 %, Table S1) than the 1Pt-7W/BN (37.8 %), on which oxygen could be easily adsorbed.

3.4. In-situ DRIFTS investigation

Although the kinetics on the 1Pt/BN and 1Pt-7W/BN catalysts differentiate reaction behaviors of the catalysts, some essential questions still need answers. For example, the nature of the active oxygen species on the 1Pt-7W/BN catalyst is unclear. Therefore, in-situ spectroscopic investigations were conducted in order to further clarify the behaviors of the catalysts and the mechanistic role of WO_3 promotion.

Considering the possibility that the adsorbed propane on the metallic Pt species could react with oxygen on either PtO_x or WO_x species, we conducted propane oxidation over 1Pt/BN and 1Pt-7W/BN catalysts in the absence of oxygen in the feed. As shown in Fig. 7a, the introduction of propane to the 1Pt/BN for 3 min results in the formation of a band at 2069 cm^{-1} assigning to linearly adsorbed CO on metallic Pt [26] and weak band at 2326 and 2378 cm^{-1} assigning to gaseous CO_2 . With the extended exposure, bands in $2800\text{--}3000\text{ cm}^{-1}$ assigning to $\delta_{\text{C-H}}$ in the gaseous C_3H_8 emerge. Some changes of the spectra with reaction time could be clearly observed. The band intensity of adsorbed CO gradually declines while those of $\delta_{\text{C-H}}$ in propane continuously increase, indicating that the propane molecules could be rapidly decomposed to CO. Meanwhile, the intensities of CO_2 reach the maximum at 7 min then decline up to 15 min. Such findings imply that CO might be intermediates in propane oxidation over the catalyst, which could be further oxidized to CO_2 . However, when the oxygen species in the catalysts are consumed, the formation of CO_2 ceases. Moreover, the CO band gradually shifts to lower wavenumber upon the exposure, probably due to combined effects of reduction of Pt oxides by propane and less CO coverage on the Pt surface, which could both cause red-shift of the band. Our DRIFTS results are in agreement with those in literature. For example, Wu et al. [17] conducted propane adsorption on the Pt/ TiO_2 catalyst, and the authors found adsorbed CO on the catalyst (although they attributed CO as the final product). The authors also revealed various surface species such as propylene, acetone and formate. However, in the current case, the bands in $1200\text{--}1800\text{ cm}^{-1}$ region are

rather weak and overlapped, which makes it very difficult to unambiguously assign these bands. Nevertheless, the possible presence of such surface intermediates and various carbonates could not be ruled out. In the case of 1Pt-7W/BN (Fig. 7b), the introduction of propane to the catalyst for 5 min results in very different spectroscopic features. Negative bands at 3688 , 3420 and 3392 cm^{-1} emerge. The assignment of these bands is confirmed by the comparison of the IR spectra of the BN, 7W/BN and 1Pt-7W/BN catalysts (Fig. S3a). It is clear that the bands at 3420 and 3392 cm^{-1} are due to the surface hydroxyl groups on the BN support, while the band at 3688 cm^{-1} is due to the surface hydroxyl groups on WO_3 . The continuous consumption of the surface hydroxyl groups in the initial stage (up to 20 min) suggests such groups may participate in the reaction, which is evidenced by the increasing intensities of the bands of CO_2 in $2300\text{--}2400\text{ cm}^{-1}$ (Fig. 7b). However, the band intensities remain constant after 20 min, implying the quantity of the hydroxyl groups are limited. Moreover, although the hydroxyl groups on BN support (bands at 3420 and 3392 cm^{-1}) are also consumed during the reaction, its role might be quite limited compared to those on the WO_3 because such groups also exist in the 1Pt/BN but with much lower catalytic activity. The consumption of surface hydroxyl groups on the 1Pt-7W/BN are also confirmed by the DRIFT spectra with the environment being taken as the background (Fig. S3b), as the bands at 3688 , 3420 and 3392 cm^{-1} continuously decline in intensities upon the exposure in propane. Another feature of these spectra is that the shapes are very different from those on the 1Pt/BN, probably due to the structural changes of the 1Pt-7W/BN catalyst by the interaction with propane. When propane was stopped and the sample was purged by N_2 , the spectra remain unchanged. However, purge with O_2 for 1 min immediately recovers the spectrum to its initial state (a flat baseline, Fig. 7b), suggesting the introduction of O_2 to the system can easily restore the structure of the catalyst. Wu et al. [17] also conducted propane adsorption on the WO_3 -promoted Pt/ TiO_2 catalyst, and they concluded that the higher intensity of the CO band on the catalyst compared to that on the Pt/ TiO_2 is a reflection of its higher activity. In the current work, obvious differences are found on the two catalysts. On the one hand, the CO band on the 1Pt/BN catalyst is absent on the 1Pt-7W/BN, probably due to its fast oxidation to CO_2 on the 1Pt-7W/BN. Indeed, the intensities of CO_2 band on this catalyst is significantly higher than those on the 1Pt/BN, implying its higher activity. On the other hand, the consumption of surface oxygen species on the 1Pt-7W/BN lasts much longer than that on the 1Pt/BN (40 min versus 15 min), due to the presence of WO_x species in the catalyst.

Fig. 8 illustrates the reaction behaviors of the catalyst in the presence of both propane and oxygen. For the 1Pt/BN catalyst (Fig. 8a), compared to the spectra in the absence of oxygen, the presence of both propane and oxygen leads to the disappearance of the adsorbed CO, suggesting the reaction between CO and O species is rather fast, which again confirms that CO could be the reaction intermediates. Also, the intensities of the gaseous CO_2 bands remain unchanged after 10 min,

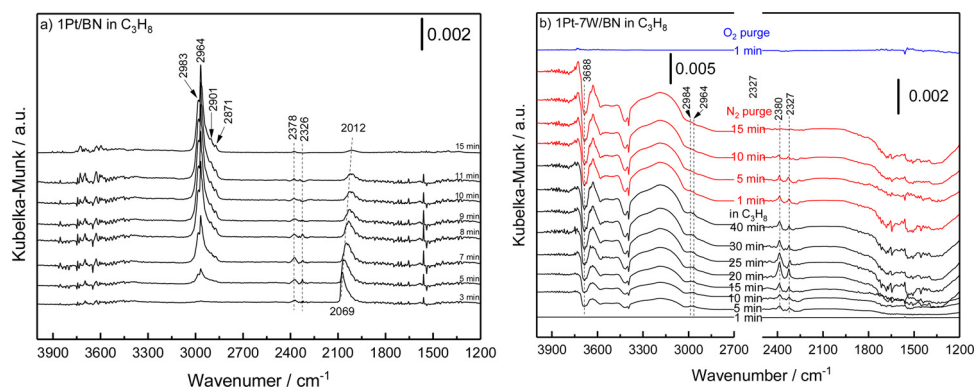


Fig. 7. In-situ DRIFT spectra of propane oxidation in the absence of oxygen over a) 1Pt/BN and b) 1Pt-7W/BN catalysts at 220°C .

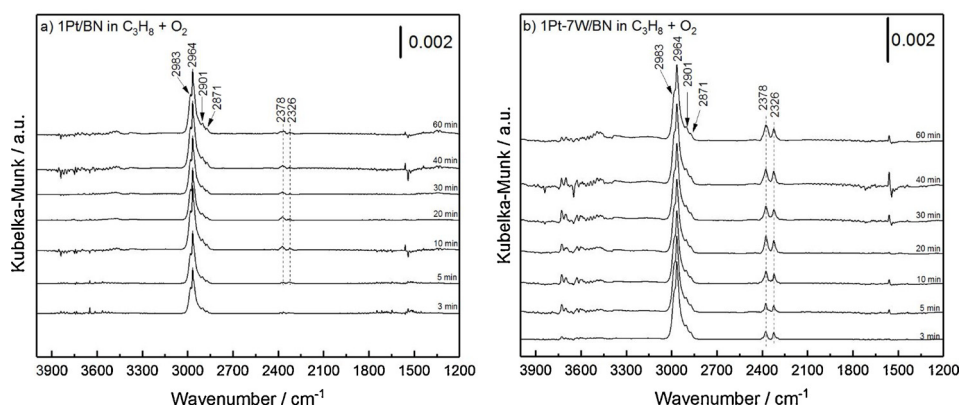


Fig. 8. In-situ DRIFT spectra of propane oxidation over a) 1 Pt/BN and b) 1 Pt-7W/BN catalysts at 220 °C.

because of the constant partial pressure of oxygen in the feed stock. In the case of 1Pt-7W/BN (Fig. 8b), it gives similar spectra as the 1Pt/BN except the band intensities for gaseous CO₂ are higher, implying its higher activity than the 1Pt/BN. Also, the structural changes of the 1Pt-7W/BN catalyst could not be observed because of the presence of oxygen in the feed, which results in fast and reversible restore of the structure, as shown in Fig. 7b. Wu et al. [26] conducted propane oxidation over Pt/Al₂O₃ and WO₃-promoted Pt/Al₂O₃ catalysts and the spectra on the two catalysts are quite similar, which leads to a conclusion that the addition of WO₃ does not change the reaction routes of propane oxidation. The authors therefore proposed that the addition of WO₃ may accelerate some RDS of the reaction (the cleavage of the C-H bond at Pt-WO₃ interface) [26].

The similar spectra obtained on the 1Pt/BN and 1Pt-7W/BN catalysts under the reaction conditions (propane and oxygen, Fig. 8) may not differentiate the behaviors of the catalysts, however, the behaviors of the catalysts in the absence of oxygen (Fig. 7) do provide some essential information on the reaction mechanisms. On the one hand, CO could be an intermediate during the reaction. On the other hand, the promoting effect of WO_x in the 1Pt/BN catalyst is due to facile reaction between the hydroxyl group on WO_x species and the C-H bond in the propane molecule, which is a kinetically essential step in deep oxidation of propane.

4. Conclusions

This work demonstrates that the addition of WO₃ in the 1Pt/BN catalyst could remarkably improve the low-temperature activity for the total oxidation of propane, which makes these catalysts quite potential in practical application. The enhanced activity could be attributed to the generation of Pt-WO_x interfacial sites for the reaction, which are more active than the Pt⁰-Ptⁿ⁺ sites (with TOF values enhanced by up to 45-fold). The kinetic results propose that the possible RDS on the W-containing catalyst might be the reaction between the propane adsorbed on metallic Pt and oxygen species on WO_x. Furthermore, the in-situ DRIFTS results illustrate that the facile reaction between the hydroxyl group on WO₃ and the C-H bond in the propane (adsorbed on metallic Pt) accounts for the enhanced activity.

Declaration of Competing Interest

None.

CRediT authorship contribution statement

Wen-Min Liao: Investigation, Methodology, Writing - original draft. **Xiu-Xiu Fang:** Formal analysis, Funding acquisition. **Bing-Heng Cen:** Data curation, Formal analysis. **Jian Chen:** Validation. **Yan-Rong Liu:** Investigation. **Meng-Fei Luo:** Conceptualization, Funding

acquisition. **Ji-Qing Lu:** Project administration, Writing - review & editing.

Acknowledgement

This work is financially supported by the National Natural Science Foundation of China (No. 21872124).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2020.118858>.

References

- [1] R.G. Derwent, R.A. Field, P. Dumitrescu, T.P. Murrells, S.P. Telling, *Atmos. Environ.* 156 (2017) 15–23.
- [2] M.N. Taylor, W. Zhou, T. Garcia, B. Solsona, A.F. Carley, C.J. Kiely, S.H. Taylor, *J. Catal.* 285 (2012) 103–114.
- [3] L. Chen, J. Hu, R. Richards, *J. Am. Chem. Soc.* 131 (2009) 914–915.
- [4] D. Munz, T. Strassner, *Inorg. Chem.* 54 (2015) 5043–5052.
- [5] R. Burch, M.J. Hayes, *J. Mol. Catal. A: Chem.* 100 (1995) 13–33.
- [6] A. Tomita, T. Miki, Y. Tai, *Appl. Catal. A: Gen.* 522 (2016) 138–144.
- [7] Y.X. Xin, H. Wang, C.K. Law, *Combust. Flame* 161 (2014) 1048–1054.
- [8] Z. Hu, Z. Wang, Y. Guo, L. Wang, Y.L. Guo, J.S. Zhang, W.C. Zhan, *Environ. Sci. Technol.* 52 (2018) 9531–9541.
- [9] Z. Wang, Z.P. Huang, J.T. Brosnahan, S. Zhang, Y.L. Guo, Y. Guo, L. Wang, Y.S. Wang, W.C. Zhan, *Environ. Sci. Technol.* 53 (2019) 5349–5358.
- [10] Z. Ren, Z.L. Wu, W.Q. Song, W. Xiao, Y.B. Guo, J. Ding, S.L. Sui, P.X. Gao, *Appl. Catal. B: Environ.* 180 (2016) 150–160.
- [11] R.P. Marin, S.A. Kondrat, R.K. Pinnell, T.E. Davies, S. Golunski, J.K. Bartley, G.J. Hutchings, S.H. Taylor, *Appl. Catal. B: Environ.* 140–141 (2013) 671–679.
- [12] B. Puértolas, A. Smith, I. Vázquez, A. Dejoz, A. Moragues, T. Garcia, B. Solsona, *Chem. Eng. J.* 229 (2013) 547–558.
- [13] W.M. Liao, P.P. Zhao, B.H. Cen, A.P. Jia, J.Q. Lu, M.F. Luo, *Chin. J. Catal.* 41 (2020) 442–453.
- [14] Y.P. Zheng, L.H. Zhang, S.L. Wang, D. Ding, H. Zhang, M.S. Chen, H.L. Wan, *Langmuir* 29 (2013) 9090–9097.
- [15] F.C. Galisteo, R. Mariscal, M.L. Granados, J.L.G. Fierro, R.A. Daley, J.A. Anderson, *Appl. Catal. B: Environ.* 59 (2005) 227–233.
- [16] J.A. Enterkin, W. Setthapun, J.W. Elam, S.T. Christensen, F.A. Rabuffetti, L.D. Marks, P.C. Stair, K.R. Poeppelmeier, C.L. Marshall, *ACS Catal.* 1 (2011) 629–635.
- [17] X.D. Wu, Z. Zhou, D. Weng, B. Wang, *J. Environ. Sci.* 24 (2012) 458–463.
- [18] C.P. O'Brien, G.R. Jenness, H. Donga, D.G. Vlachos, I.C. Lee, *J. Catal.* 337 (2016) 122–132.
- [19] Y.R. Liu, X. Li, W.M. Liao, A.P. Jia, Y.J. Wang, M.F. Luo, J.Q. Lu, *ACS Catal.* 9 (2019) 1472–1481.
- [20] Y. Yazawa, H. Yoshida, S.I. Komai, T. Hattori, *Appl. Catal. A: Gen.* 233 (2002) 113–124.
- [21] G. Corro, J.L.G. Fierro, V.C. Odilon, *Catal. Commun.* 4 (2003) 371–376.
- [22] H. Luo, X.D. Wu, D. Weng, S. Liu, R. Ran, *Rare Met.* 36 (2017) 1–9.
- [23] M. García-Diéguez, Y. Chin, E. Iglesia, *J. Catal.* 285 (2012) 260–272.
- [24] X. Li, Y.R. Liu, W.M. Liao, A.P. Jia, Y.J. Wang, J.Q. Lu, M.F. Luo, *Appl. Surf. Sci.* 475 (2019) 524–531.
- [25] T. Garcia, S. Agouram, S.H. Taylor, D. Morgan, A. Dejoz, I. Vázquez, B. Solsona, *Catal. Today* 254 (2015) 12–20.
- [26] X.D. Wu, L. Zhang, D. Weng, S. Liu, Z.C. Si, J. Fan, *J. Hazard. Mater.* 225–226 (2012) 146–154.

- [27] W. Mao, Y.B. Bai, B. Wang, W. Wang, H. Ma, Y. Qin, C. Li, J. Lu, Z.W. Liu, *Appl. Catal. B: Environ.* 206 (2017) 65–73.
- [28] H.L. Wang, M.H. Liu, Y. Ma, K. Gong, W. Liu, R. Ran, D. Weng, X.D. Wu, S. Liu, *ACS Catal.* 8 (2018) 2796–2804.
- [29] M. Yang, X.C. Zhao, Y.J. Wang, N. Lei, A.Q. Wang, T. Zhang, *Chinese J. Catal.* 39 (2018) 1027–1037.
- [30] G.J. Shi, J.Y. Xu, Z.G. Song, Z. Cao, K. Jin, S.H. Xu, X.T. Yan, *Mol. Catal.* 456 (2018) 22–30.
- [31] C.A. Lin, J.C.S. Wu, J.W. Pan, C.T. Yeh, *J. Catal.* 210 (2002) 39–45.
- [32] T.M. Tran-Thuy, C.C. Chen, S.D. Lin, *ACS Catal.* 7 (2017) 4304–4312.
- [33] A. Pakdel, Y. Bando, D. Golberg, *Chem. Soc. Rev.* 43 (2014) 934–959.
- [34] S. Lin, X.X. Ye, R.S. Johnson, H. Guo, *J. Phys. Chem. C* 117 (2013) 17319–17326.
- [35] S.H. Zhu, X.Q. Gao, Y.L. Zhu, J.L. Cui, H.Y. Zheng, Y.W. Li, *Appl. Catal. B: Environ.* 158–159 (2014) 391–399.
- [36] W. Li, K.B. Chi, H. Liu, H.J. Ma, W. Qu, C.X. Wang, G. Lv, *Appl. Catal. A: Gen* 537 (2017) 59–65.
- [37] K.S. Song, H.B. Zhang, Y.H. Zhang, Y. Tang, K.J. Tang, *J. Catal.* 299 (2013) 119–128.
- [38] R. Kourieh, S. Bennici, M. Marzo, A. Gervasini, A. Auroux, *Catal. Commun.* 19 (2012) 119–126.
- [39] J.L.G. Fierro, J.M. Palacios, F. Tomas, *Surf. Interface Anal.* 13 (1988) 25–32.
- [40] J.P. Contour, G. Mouvier, M. Hoogewys, C. Leclerc, *J. Catal.* 48 (1977) 217–228.
- [41] G.M. Bancroft, I. Adams, L.L. Coatsworth, C.D. Bennewitz, J.D. Brown, W.D. Westwood, *Anal. Chem.* 47 (1975) 586–588.
- [42] T.H. Fleisch, G.W. Zajac, J.O. Schreiner, G.J. Mains, *Appl. Surf. Sci.* 26 (1986) 488–497.
- [43] M.M. Sun, S.N. Wang, Y.S. Li, H.D. Xu, Y.Q. Chen, *Appl. Surf. Sci.* 402 (2017) 323–329.
- [44] J.A. Enterkin, W. Setthapun, J.W. Elam, S.T. Christensen, F.A. Rabuffetti, L.D. Marks, P.C. Stair, K.R. Poeppelmeier, C.L. Marshall, *ACS Catal.* 1 (2011) 629–635.
- [45] B. Wang, X.D. Wu, R. Ran, Z.C. Si, D. Weng, *J. Mol. Catal. A: Chem.* 356 (2012) 100–105.
- [46] R. Burch, M.J. Hayes, *J. Mol. Catal. A: Chem.* 100 (1995) 13–33.
- [47] L.F. Liotta, *Appl. Catal. B: Environ.* 100 (2010) 403–412.
- [48] C. Kokkofitis, M. Stoukides, *J. Catal.* 243 (2006) 428–437.
- [49] M.S. Avila, C.I. Vignatti, C.R. Apesteguía, T.F. Garetto, *Chem. Eng. J.* 241 (2014) 52–59.
- [50] K. Otto, J.M. Andino, C. Parks, *J. Catal.* 131 (1991) 243–251.
- [51] T.F. Garetto, C.R. Apesteguía, *Catal. Today* 62 (2000) 189–199.
- [52] M. Aryafar, F. Zaera, *Catal. Lett.* 48 (1997) 173–183.
- [53] M.P. Heynderickx, J.W. Thybaut, H. Poelman, D. Poelman, G.B. Marin, *Appl. Catal. B: Environ.* 95 (2010) 26–38.
- [54] T. Garetto, E. Rincón, C.R. Apesteguía, *Appl. Catal. B: Environ.* 48 (2004) 167–174.