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# Total oxidation of propane on $Pt/WO_x/Al_2O_3$ catalysts by formation of metastable $Pt^{\delta^+}$ species interacted with $WO_x$ clusters

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# HIGHLIGHTS

#### GRAPHICAL ABSTRACT

► The activity of  $Pt/Al_2O_3$  catalyst for  $C_3H_8$  oxidation is promoted by  $WO_x$  addition. ► The  $Pt^{\delta^+}/Pt$  ratio increases with  $WO_x$  surface density. ► The reducibility of metastable  $Pt^{\delta^+}$  species correlates with the catalytic activity. ► simple redox model is presented involving the initial C—H bond activation.

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# 1. Introduction

Diesel engine vehicles have been rising rapidly in worldwide due to their high fuel efficiency, reliability and durability compared to gasoline cars [1]. Consequently, diesel exhaust pollutions are leading to increasingly stringent emission standards. Besides particulate matter (PM) and nitrogen oxides ( $NO_x$ ), diesel emissions also contain a large share of unburned hydrocarbons (HC) presented in both the gas and particle phases [2]. These compounds



# ABSTRACT

A series of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts with various tungsten oxide loadings were prepared by a stepwise wet impregnation method. The catalysts were characterized by X-ray diffraction, nitrogen physisorption, Raman, UV–vis diffuse reflectance, transmission electron microscopy and infrared spectroscopy of adsorbed probe molecules (CO, NH<sub>3</sub> or C<sub>3</sub>H<sub>8</sub>). The propane oxidation activity of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst is significantly improved by the addition of tungsten oxide. The tungsten oxide overlayer is presented as monomeric/polymeric WO<sub>x</sub> clusters and WO<sub>3</sub> crystals depending on the loading amount. The most active catalyst occurs at an intermediate surface tungsten density corresponding to the maximum of polytungstate species. The electronic interactions between Pt and WO<sub>x</sub> clusters lead to the generation of more reducible Pt<sup> $\delta$ +</sup> species which are suggested to be active sites for propane oxidation. Basically, a simple model is proposed involving the initial C–H bond activation at the platinum–tungsten oxide interface.

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when oxidized produce a wide variety of oxygenated products including aldehydes, ketones, alcohols, phenols, etc. most of which have been proven toxicity, and play a significant role in ozone production in the presence of nitrogen oxides [3]. For the reduction of HC emission as well as CO and the soluble organic fraction (SOF) of PM, Pt/Al<sub>2</sub>O<sub>3</sub> system as a typical diesel oxidation catalyst (DOC) has been widely applied in current commercial oxidation catalysts installed in diesel driven vehicles [4]. Almost 60–80% of total hydrocarbon emissions are produced in the cold-start period [5]. Generally, the efficient oxidation of saturated hydrocarbons on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst requires relative high temperatures. It is therefore important to find routes to improve the low-temperature oxidation activity of platinum catalysts.

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The oxidation activity of Pt catalysts is found to depend strongly on the oxidation state and dispersion of platinum, both of which can be affected by the supports and additives. H. Yoshida's group investigated the effect of supports (MgO, La<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, SiO<sub>2</sub>,  $SiO_2-Al_2O_3$  and  $SO_4^{2-}-ZrO_2$ ) on the low-temperature propane combustion over platinum catalysts [6-8]. They found that the turnover frequency is improved with the increase in the acid strength of support materials at the same dispersion of platinum. Kim et al. also ascribed the large different activities of Pt/ZrO<sub>2</sub>-SiO<sub>2</sub> and Pt/ZrO<sub>2</sub>-SiO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> catalysts, despite their close platinum dispersion, to the effect of the acidity generation on propane combustion [9]. On the other hand, Burch's group found that the alumina modified with fluorine is more acidic than that with sulfur dioxide, but its combustion activity is not higher than the latter one [10]. Similarly, Hubbard et al. reported no enhanced activity with sulfated zirconia even though the acidity increased by 11 orders of magnitude [11]. So it seems that the total acidity of the support is not the only important factor in determining the propane combustion activity of platinum catalysts.

Solid oxide additives are promising for preparing highly active platinum catalysts. For example, the propane oxidation turnover rate on Pt/V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts increases with the vanadium oxide loading, probably because the intrinsic Pt oxidation activity increases with the sample acidity in spite of increased Pt dispersion [12]. The increased activity for propane combustion on Pd/V<sub>2</sub>O<sub>5</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts is also related to the modified redox properties of the catalysts and in particular the high reducibility of vanadium species [13]. The promoting effect of tungsten oxide on the propane oxidation activity of platinum catalysts has been also reported. Yoshida's group [8,14] showed that the enhanced activity of catalysts is ascribed to less oxidized platinum by interaction with the electronegative additives used (W, V, P, Mo and Nb) under the oxidizing atmosphere. The stabilities of  $Pt/WO_x/Al_2O_3$ and  $Pt/WO_x/TiO_2-SiO_2$  are proved stable on the propane combustion tests at 750 °C for 1000 h [15] and at 350 °C for 400 h [16]. A similar promotion effect of tungsten oxide was found on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst for methane combustion [17]. Recently, Taylor's groups ascribed the enhanced catalytic activity of Pd/WO<sub>x</sub>/TiO<sub>2</sub> catalyst to an increased concentration of highly reactive oxygen species on the new WO<sub>x</sub>-decorated interface between PdO<sub>x</sub> and TiO<sub>2</sub> particles [18]. They also found that there is significance in the order of impregnation of the noble metal and promoter on the final performance of for  $Pd/VO_x/Al_2O_3$  catalysts [19]. The formation of active sites at the Pt/WO<sub>x</sub> interface on titania was reported to facilitate the dissociation of surface intermediates for propane oxidation in our previous study [20]. Nevertheless, the catalytic behaviors of such catalysts are not fully understood; for example, the nature of the true active phase, metal or metal oxide, remains a matter of discussion. A detailed characterization study needs to be performed to elucidate the exact nature of the metal/support interaction between platinum and tungsten oxide and the corresponding effect on propane combustion activity.

In this study, the effect of different tungsten oxide loadings on the propane oxidation of  $Pt/Al_2O_3$  was investigated by using structural characterizations and *in-situ* diffuse reflectance infrared transform (DRIFT) spectroscopy. The key factors controlling the activity of the catalysts were discussed from the viewpoint of Pt dispersion, Pt oxidation state and reactivity of Pt sites affected by tungsten oxide, and a simple reaction scheme was proposed.

#### 2. Experimental

# 2.1. Catalyst preparation

The alumina supports modified with various weight percentages of tungsten oxide (10 wt.%, 20 wt.% and 30 wt.%, calculated in terms of WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) were prepared by the incipient-wetness impregnation of  $\gamma$ -alumina (BASF, Germany,  $S_{BET} = 150 \text{ m}^2/\text{g}$ ) with ammonium metatungstate ((NH<sub>4</sub>)<sub>10</sub>W<sub>12</sub>O<sub>41</sub>·5H<sub>2</sub>O, 99.5%, Yili, China). After drying at 110 °C for 12 h, the samples were calcined at 550 °C for 3 h in a muffle and the obtained WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> supports were denoted as *y*WAl (where *y* was the loading percentage of WO<sub>3</sub>). For reference, pure tungsten oxide (derived by decomposition of ammonium metatungstate) and alumina were treated by the same calcination process.

The supported catalysts were prepared by impregnating the obtained supports (*y*WAl,  $Al_2O_3$  and  $WO_3$ ) with  $Pt(NO_3)_2$  solution (27.82 wt.%, Heraeus) as the precursor. The nominal loading amount of Pt was 1 wt.%. The impregnation procedure was the same as described above. The impregnated powders were submitted to drying at 110 °C for 12 h and calcination at 500 °C for 3 h in static air. The received catalysts were denoted as *y*PtWAl,  $Pt/Al_2O_3$  and  $Pt/WO_3$ , respectively.

## 2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns were determined by a Japan Science D/max–RB diffractometer employing Cu K $\alpha$  radiation ( $\lambda$  = 0.15418 nm) operating at 40 kV and 30 mA.

Textural properties were determined by nitrogen physisorption at -196 °C using a JW-BK122F (Beijing JWGB, China) instrument. Prior to nitrogen physisorption measurement, the samples were degassed to 0.01 Pa at 220 °C. The specific desorption pore volume was assessed by the Barrett–Joyner–Halenda (BJH) method.

The Raman spectra of the samples were obtained at ambient condition on a confocal micro-Raman apparatus (LabRam HR 800, Horiba Jobin Yvon, France) with a CCD detector.UV–vis diffuse reflectance spectra (UV–vis DRS) of the samples were recorded on a Hitachi U-3010 (Japan) spectrophotometer equipped with an integrating sphere.

Transmission electron microscope (TEM) images were taken using a FEI Tecnai  $G^2$  20 with an acceleration voltage of 200 kV.

Infrared (IR) spectra of CO adsorption were recorded on a Nicolet 6700 FTIR spectrometer equipped with a MCT detector. Successive experiments were carried out to collect the information of CO adsorption for the catalysts. After pretreating in He (100 ml/min) at 500 °C for 1 h, the as-received catalyst was cooled down to RT for CO adsorption. After the first CO adsorption, the catalyst was then treated in 5%  $O_2$ /He (100 ml/min) at 500 °C for 1 h to obtain the oxidized sample, and was cooled down to RT in He (100 ml/min) for the second CO adsorption. Similarly, the reduction treatment was then performed in 5% CO/He (100 ml/min) at 500 °C before the third CO adsorption. For each CO adsorption measurement, the sample wafer was first exposed to 1% CO/He stream (100 ml/min) for 20 min and then flushed with He for 20 min. IR spectra were recorded under He stream by accumulating 32 scans at a resolution of 4 cm<sup>-1</sup>.

IR spectra of ammonia adsorption were recorded on the same apparatus. The catalyst was purged by nitrogen at 500 °C for 30 min. A gas mixture of 1000 ppm  $NH_3/N_2$  was dosed in a diffuse reflectance IR cell at RT for 30 min, and then the catalyst was flushed with  $N_2$ . The spectra were collected by accumulating 32 scans at a resolution of 4 cm<sup>-1</sup>.

IR spectra of propane oxidation were performed on the same apparatus. After pretreatment in nitrogen at 500 °C for 0.5 h, the catalyst was cooled down to 200 °C. The spectra were recorded at an interval of 50 °C after exposing the catalyst to 800 ppm  $C_3H_8/2\%$   $O_2/N_2$ . The heating rate was 10 °C/min.



Fig. 1. Propane oxidation activities of  $\text{Pt}/\text{Al}_2\text{O}_3$  and the tungsten oxide modified catalysts.

#### 2.3. Activity measurement

The activities of the catalysts for propane oxidation were tested in a fixed bed reactor made of stainless steel (i.d. 18 mm). Two hundred milligrams of catalyst powders (diluted to 1 ml with silica pellets), sandwiched between two quartz wool layers, were inserted into the reactor. After a pretreatment at 500 °C in N<sub>2</sub> for 30 min and being cooled down to RT, the reactor was heated to 500 °C at a rate of 10 °C/min. The gas mixture consisted of 800 ppm C<sub>3</sub>H<sub>8</sub>, 2% O<sub>2</sub> and N<sub>2</sub> in balance with a total flow rate of 1000 ml/min. The outlet gas concentrations were determined by a MKS 2300 IR spectrometer.

# 3. Results

#### 3.1. Activities for propane oxidation

Fig. 1 shows the propane oxidation activities of  $Pt/WO_x/Al_2O_3$ catalysts. The propane catalytic oxidation of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst at low temperatures is significantly promoted by the modification of tungsten oxide depending on the loading amount. The  $T_{50}$  (the temperature for 50% propane conversion) follows the order of 30PtWAl  $\approx$  20PtWAl(245 °C) < 10PtWAl(268 °C) < Pt/Al<sub>2</sub>O<sub>3</sub> (327 °C). The shift of the  $T_{50}$  towards lower temperatures exceeds 80 °C when the tungsten oxide loading reaches 20 wt.%. A further increase in the tungsten oxide loading makes no contribution to the activity of platinum catalysts. It is probably more meaningful to compare the  $T_{10}$  values (the temperature for 10% propane conversion) since propane oxidation is a highly exothermic reaction and the heat and mass transfer limitations are small at low temperatures. They obey a similar sequence: 20PtWAl (200 °C) < 30PtWAl  $(204 \circ C) < 10$  PtWAl  $(210 \circ C) <$ Pt/Al<sub>2</sub>O<sub>3</sub>  $(240 \circ C)$ . The most active catalyst is 20PtWAl, which has a much higher activity than the tungsten-free Pt/Al<sub>2</sub>O<sub>3</sub> catalyst with a  $T_{10}$  shift towards lower temperatures by 40 °C.

#### 3.2. Solid properties

Fig. 2 shows the XRD patterns of the catalysts. All the samples exhibit characteristic peaks of  $\gamma$ -alumina. No diffraction peaks of crystalline WO<sub>3</sub> are observed for 10PtWAl, indicating the formation of uniformly spread oxotungsten species. Typical diffraction peaks ( $2\theta$  = 23.74°, 28.81°, 33.67°, 41.58°, 50.35°, 54.82° and 60.35°) of bulk tungsten oxide, identified as orthorhombic WO<sub>3</sub> (JCPDS card 20-1324), are observed on 20PWAl and 30PWAl. There are



Fig. 2. XRD patterns of the (1)  $Pt/Al_2O_3,$  (2) 10PtWAl, (3) 20PtWAl and (4) 30PtWAl catalysts.

able 1	
tructural and textural properties of the catalysts.	

Catalysts	Pt (wt.%)	WO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> (wt.%)	$S_{\text{BET}} (m^2/g)$	Pore volume (cm <sup>3</sup> /g)
$Pt/Al_2O_3$	1	0	142	0.47
10PtWAl	1	10	135	0.41
20PtWAl	1	20	127	0.39
30PtWAl	1	30	117	0.35

no significant diffraction peaks of metallic or oxidized Pt phase, indicating a high dispersion of the metal on all the catalysts.

As listed in Table 1, the surface area of the catalysts decreases slightly with increasing the tungsten oxide loading, which would not result in any obvious difference of the catalytic performance. Fig. 3 shows the pore diameter distributions of the catalysts. The main feature is the appearance of a bimodal distribution in pore diameter of the catalyst with increasing the tungsten oxide loading. All the catalysts yield a pore diameter distribution at 8–9 nm, almost independent of the tungsten oxide loading, which is assigned to the pore structure of the alumina support. A second contribution at a larger pore diameter appears especially on 30PtWAl, which is associated to the surface layer of bulk WO<sub>3</sub>.



Fig. 3. Pore size distribution of Pt/WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts.

 Table 2

 Characteristics of WO<sub>x</sub> species on the catalysts.

Catalysts	$ ho_{\rm W,surf}({\rm W}/{\rm nm^2})$	$D_{WO_3} (nm)^a$	$E_{\rm g}~({\rm eV})^{\rm b}$
$Pt/Al_2O_3$	-	-	-
10PtWAl	1.9	-	3.83
20PtWAl	4.0	2.9(3)	3.75
30PtWAl	6.9	5.3(7)	3.62
20WAl	4.0	2.6(4)	4.05

<sup>a</sup> Calculated by Williamson-Hall equation from the XRD data.

<sup>b</sup> Determined by applying UV-vis spectra and Kubelka-Munk function multiplied by the photon energy.



Fig. 4. Raman spectra of the catalysts and supports.

# 3.3. Raman and UV-vis

The tungsten oxide species are different on the alumina support as a function of surface WO<sub>x</sub> density (W atoms per nm<sup>2</sup> Al<sub>2</sub>O<sub>3</sub>): surface monotungstate WO<sub>4</sub> species, surface polytungstate WO<sub>5</sub>/WO<sub>6</sub> species and WO<sub>3</sub> crystals. It has been seen from the XRD patterns that crystalline WO<sub>3</sub> appears on 20PtWAl and especially 30PtWAl catalysts. Table 2 shows the mean crystallite sizes of WO<sub>3</sub> in these two samples. Obviously, a larger crystallite size of WO<sub>3</sub> is formed on the latter catalyst due to the aggregation and sintering of WO<sub>3</sub>. To further illuminate such a transformation of WO<sub>x</sub> clusters to WO<sub>3</sub> crystallites, the Raman spectra of the W-containing catalysts were recorded in the 200–1200 cm<sup>-1</sup> region and the results are shown in Fig. 4. It is known that the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support has no Raman active modes. The spectrum of WO<sub>3</sub> reveals typical bands at 800, 700 and 250 cm<sup>-1</sup> which are assigned to W–O stretching, W-O bending and W-O-W deformation modes of octahedrally coordinated WO<sub>3</sub> crystals [21]. The band at  $320 \text{ cm}^{-1}$  is a consequence of the appreciable distortion of the WO<sub>3</sub> structure from the ideal octahedral arrangement of ReO3-type structure, and may be assigned to the W-O bending mode in the tetrahedrally coordinated tungstate. At a low tungsten oxide loading (10 wt.%), only a band at 1015 cm<sup>-1</sup> is observed assigned to symmetric W=O stretching arising from tetrahedrally coordinated surface species. When the tungsten oxide loading is enhanced to 20 wt.%, the W-O bands associated with WO<sub>3</sub> crystals appear in a low intensity, implying the occurrence of aggregation and crystallization of tungsten oxide locally on 20PtWAl catalyst. WO3 crystals become one of major phases on 30PtWAl catalyst, which is consistent with the XRD result.

The band corresponding to W=O vibrations of polytungstate appears at  $970 \text{ cm}^{-1}$  for the modified alumina support (20 wt.% WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>), which has been assigned to the symmetric stretching

vibration mode of W=O bonding in two-dimensional oxotungsten species in interaction with the support. This band shifts towards to a higher wavenumber at  $1015 \text{ cm}^{-1}$  for all PtWAI catalysts. Such a shift has been reported as differences in the degree of dehydration of tungsten species and also as a consequence of a greater lateral interaction [22]. In our work, it is more likely that the interaction between platinum and surface tungsten oxide species affects the distortion of the oxotungsten species, which was also found over Pd/WO<sub>x</sub>/TiO<sub>2</sub> system by Taylor's group [18]. It appears that the transfer of electrons from the metallic Pt to the electronegative additives (WO<sub>x</sub>, where 2 < x < 3) at the Pt–WO<sub>x</sub> interface makes the W=O bond stronger, resulting in a blue shift of the W=O Raman band.

Further investigation was done by applying UV-vis diffuse reflectance spectroscopy and Kubelka-Munk function multiplied by the photon energy. As listed in Table 2, the  $E_{\rm g}$  value continuously decreases from 3.83 to 3.62 eV with increasing the surface W density, indicating the growth of  $WO_x$  domains at higher surface densities. Again, the electronic interaction between platinum and tungsten oxide is evidenced by the decrease of  $E_{g}$  after impregnation of platinum (20PtWAl vs. 20WAl), which reflects the degree of electron delocalization in the tungsten oxide phase. It is known from Table 2 that the small increase in the crystallinity of WO<sub>3</sub> crystals should not result in such a significant difference of the  $WO_x$  absorption edge energy. It is more plausible that the effective charge delocalization of Pt by WO<sub>x</sub> domains may introduce an additional electronic density for tungsten oxide and correspondingly the generation of electron deficient active sites (such as  $Pt^{\delta^+}$ ) on the catalysts [23].

# 3.4. TEM

Hydrocarbon oxidation on platinum group metal catalysts is sometimes speculatively classified in structure-sensitive reactions preferentially promoted on larger precious metal crystallites [6,24,25]. Fig. 5 shows the TEM images of the catalysts. No obvious difference is observed among the catalysts with or without WO<sub>3</sub> addition. All the catalysts seem to show a high dispersion of platinum with diameters located in a narrow range of 1-2 nm. Although the TEM images do not allow on the clear discrimination between the small clusters of Pt and WO<sub>3</sub> particles, few dark particles larger than 3 nm are observed, indicating no obvious difference in the Pt particle size of the catalysts. It implies that the variation in the oxidation activity of the catalysts is not due to the Pt particle size effect but due to the chemical modification of platinum species by the electronegative additives, probably the variation in the oxidation state of platinum.

## 3.5. IR spectra of CO adsorption

In order to study the reducibility of platinum species on different catalysts, successive oxidation/reduction pretreatments were performed prior to CO adsorption. Fig. 6 shows the IR spectra of the as-received, oxidized and reduced catalysts from contact with CO. Three overlapped bands at 2065, 2087 and 2107 cm<sup>-1</sup> are observed on Pt/Al<sub>2</sub>O<sub>3</sub> in Fig. 6a, which are assigned to linear CO absorbed on the terrace and step sites on platinum particles (Pt<sup>0</sup>) and partially oxidized platinum (Pt<sup> $\delta$ +</sup>) sites, respectively [26]. The bands for CO associated with terrace sites of Pt<sup>0</sup> and Pt<sup> $\delta$ +</sup> increase slightly in intensity after the oxidation treatment. The reduction pretreatment results in the disappearance of partially oxidized platinum species and a decrease in the amount of terrace sites on Pt particles. Thus, the reduction of Pt on Pt/Al<sub>2</sub>O<sub>3</sub> is more feasible than the oxidation of the catalyst, and only a small amount of reducible Pt<sup> $\delta$ +</sup> species are observed.



Fig. 5. TEM images of (a) Pt/Al<sub>2</sub>O<sub>3</sub>, (b) 10PtWAl, (c) 20PtWAl and (d) 30PtWAl catalysts.

It can be seen in Fig. 6b-d that all the bands shift to higher wavenumbers with increasing the tungsten oxide loading. For 30PtWAl catalyst, the bands associated with CO-Pt<sup>0</sup> (terrace sites), CO-Pt<sup>0</sup> (step sites) and CO-Pt<sup> $\delta$ +</sup> shift to 2078, 2098 and 2123 cm<sup>-1</sup>, respectively. It is generally related to the acidic nature of the  $WO_{x}$ modified support, which will be discussed in the next section. A second effect of WO<sub>x</sub> modification is the introduction of more reducible  $Pt^{\delta^+}$  species. The band assigned to CO coordinated to  $Pt^{\delta^+}$ sites turns to be much more intense on the as-received PtWAl catalysts, indicating that platinum species on the acidic  $WO_x/Al_2O_3$ supports are more electron-deficient than those on the electroneutral Al<sub>2</sub>O<sub>3</sub> support. More importantly, the metastable Pt<sup> $\delta^+$ </sup> species are more liable to the atmosphere on PtWAl catalysts, which correlates with our previous findings about the formation of more reducible  $Pt^{\delta^+}$  by interaction between platinum and the acidic sulfate additives on Pt/Ce<sub>0.67</sub>Zr<sub>0.33</sub>O<sub>2</sub> catalyst [27]. The number of Pt–O bonds of lower binding energy, i.e. the site density of more reactive surface oxygen, increases on the  $Pt-WO_x$  interface.

# 3.6. $NH_3$ adsorption

In order to evidence the modification of tungsten oxide on the acidity of Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, the IR spectra obtained after NH<sub>3</sub> adsorption are shown in Fig. 7. According to the literatures [28,29], typical bands at 3390, 3270 and 3183 cm<sup>-1</sup> are assigned to  $\upsilon_{as}(N-H)$ ,  $\upsilon_{s}(N-H)$  and  $\delta_{as}(NH)$  of Lewis-bound ammonia, respectively. The bands at 1260 and 1125 cm<sup>-1</sup> are corresponding to the symmetric deformation mode of ammonia coordinated to Lewis acid sites. A combination band of the symmetric and antisymmetric deformation vibration of NH<sup>4+</sup> species arises at 3022 cm<sup>-1</sup>. The broad band at 2788 cm<sup>-1</sup> is associated with the overtone of  $\delta_{as}$ (NH) of Brønsted-bound ammonia. The bands at 1682 and 1448 cm<sup>-1</sup> are characteristic of asymmetric and symmetric deformation modes of the protonated NH<sub>3</sub> (NH<sup>4+</sup>) coordinated to Brønsted acid sites. These bands decrease in intensity significantly on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst due to the electroneutral nature of alumina. Thus, the modification of tungsten oxide introduces abundant Lewis and Brønsted sites on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, and Brønsted-bound ammonia is more labile. The band at 1020 cm<sup>-1</sup> is related to the OH-bending vibration of alumina [30]. It turns to be much more intense for the WO<sub>x</sub>-modified catalysts due to the fundamental overtone of the W=O stretching mode of surface wolframyl species [29].

# 3.7. IR spectra of $C_3H_8$ oxidation

Fig. 8 shows the DRIFT spectra in the ranges of 4000–2800 and  $1700-1300 \text{ cm}^{-1}$  recorded while exposing the catalysts to propane and O<sub>2</sub> at 200–500 °C. A band at 1636 cm<sup>-1</sup> and a shoulder at 1617 cm<sup>-1</sup> due to C=C stretching, together with other weak bands at 1458 and 1375 cm<sup>-1</sup> associated to the asymmetric and symmetric –CH<sub>3</sub> deformation [31], are observed on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst after propane adsorption at 200 °C in Fig. 8a. The band at 2969 cm<sup>-1</sup> is characteristic of the C–H vibrations of gaseous propane. The bands assigned to carboxylate (acetate, 1575, 1543, 1458 and 1435 cm<sup>-1</sup>;



Fig. 6. IR spectra of the adsorbed species from contact with CO on the (a)  $Pt/Al_2O_3$ , (b) 10PtWAl, (c) 20PtWAl and (d) 30PtWAl catalysts at RT.

formate, 1590, 1558, 1386 and 1375 cm<sup>-1</sup>) become more intense with increasing the temperature. The above bands assigned to the oxygenated intermediates reach the maximum at 350 °C and then decline at higher temperatures. The variations of the bands associated with carbonaceous species (mono- or poly-dentate carbonate, 1520, 1473 and 1352 cm<sup>-1</sup>; carboxylate, 1507 and 1396 cm<sup>-1</sup>)



Fig. 7. IR spectra of the adsorbed species from contact with ammonia on the (1)  $Pt/Al_2O_3$ , (2) 10PtWAl, (3) 20PtWAl and (4) 30PtWAl catalysts at RT.

follow a similar trend [32,33]. Meanwhile, a band at  $3540 \text{ cm}^{-1}$  arises from surface OH groups on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The bands at 2969, 1636, 1617, 1458 and 1375 cm<sup>-1</sup>, due to physisorbed propane, become slightly weaker on 20PtWAl catalyst in Fig. 8b, implying that the adsorption of propane on catalyst



**Fig. 8.** IR spectra of the adsorbed species from contact with  $C_3H_8$  and  $O_2$  on the (a) Pt/Al<sub>2</sub>O<sub>3</sub> and (b) 20PtWAl catalysts at (1) 200, (2) 250, (3) 300, (4) 350, (5) 400, (6) 450 and (7) 500 °C at a heating rate of 10 °C/min.



Fig. 9. Brønsted acidity and Lewis acidity as a function of WO<sub>x</sub> surface density.

is not obviously affected by the addition of tungsten oxide. However, the bands assigned to the adsorbed oxygenated intermediates (acetate and formate) are much weaker and reach the maximum at about 300 °C. No special intermediates are observed, implying that the modification of tungsten oxide does not change the general reaction mechanism for propane oxidation, but it may accelerate some rate-determining steps of reaction and the deep oxidation of the oxygenated intermediates at lower temperatures. It is also noted that the desorption of byproducts such as hydroxyl group and carbonaceous species is promoted on the acidic catalyst.

# 4. Discussion

#### 4.1. Surface acidity, Pt oxidation state and WO<sub>x</sub> surface density

It is shown from the XRD, Raman and UV-vis results that the molecular structures of tungsten oxide phase on Pt/Al<sub>2</sub>O<sub>3</sub> catalysts include monotungstate/polytungstate surface WO<sub>x</sub> species below monolayer surface coverage ( $<4.0 \text{ W/nm}^2$ ) and crystalline WO<sub>3</sub> nanoparticles ( $\geq$ 4.0 W/nm<sup>2</sup>), which depend the loading amount. Tungsten oxide acts as a typical acidic oxide additive. Fig. 9 shows the dependencies of the amounts of Brønsted and Lewis acid sties on the WO<sub>x</sub> surface density. The normalized acidities were determined from integration of the infrared bands corresponding to NH<sub>3</sub> adsorbed on Brønsted acid sites (centered at 1473 cm<sup>-1</sup>) and Lewis acid sites (at  $1260 \text{ cm}^{-1}$ ) in Fig. 7, and were normalized by the intensity of IR bands at 1448 and 1245 cm<sup>-1</sup> for Pt/Al<sub>2</sub>O<sub>3</sub> as internal standards. The additional Lewis acid sites arise mainly from coordinatively unsaturated  $W^{x+}$  cations in  $[WO_6]$  and  $[WO_4]$ , or coordinatively unsaturated Al<sup>x+</sup> atoms as a result of the electron withdrawing nature of isolated  $W^{6+}$  atoms forming exposed  $WO_x$ groups [34,35]. The limited availability of electron-deficient W<sup>x</sup> restricts further increase in the amount of Lewis acid sites at higher  $WO_x$  surface density. Thus, it obeys a parabolic line law. Meanwhile, the Brønsted acid sites arise from partially hydrated tungsten species, including OH groups associated with W=O, W-O-W and Al–O–W linkages in WO<sub>x</sub> clusters and WO<sub>3</sub> nanoparticles. As a result, a guasi-linear function is observed.

It is known that the interaction between tungsten oxide and platinum can make the latter in more electron deficient state, which is caused by the withdrawing effect of the electronegative additives. Fig. 10 shows the variation of the partially oxidized platinum ( $Pt^{\delta+}$ ) ratio as a function of the WO<sub>x</sub> surface density. The  $Pt^{\delta+}/Pt$  ratio was calculated from division of the infrared bands corresponding to CO adsorbed on all platinum sites by that adsorbed on  $Pt^{\delta+}$  sites in Fig. 6. Clearly, the addition of WO<sub>x</sub> leads to a quasi-linear increase of the  $Pt^{\delta+}/Pt$  ratio. It is difficult to directly relate the oxidation state of Pt species to the acidity of catalyst. The interaction between platinum and tungsten oxide would lead to a proton transfer from



Fig. 10. Oxidation state of surface Pt as a function of WO<sub>x</sub> surface density.



**Fig. 11.** Propane oxidation activity and reducibility of  $Pt^{\delta+}$  as a function of the tungsten oxide loading.

the acidic surface –OH groups (Brønsted acid–base interaction) to platinum species [36]. The coordinatively unsaturated  $Pt^{\delta+}$  cations can be also formed as a result of the electron withdrawing nature of isolated W<sup>6+</sup> atoms forming exposed WO<sub>x</sub> groups (Lewis acid–base interaction). It should be also noted that the acidity of catalyst can affect the carbon accumulation, which is a critical issue in propane oxidation over platinum catalysts and remains to be studied in the future.

#### 4.2. Reducibility of platinum and propane oxidation activity

It is seen in Fig. 1 that the oxidation activity of catalysts does not increase quasi-linearly when the tungsten oxide loading exceeds 20 wt.%, suggesting that the surface  $Pt^{\delta+}/Pt$  ratio is not the exact factor in determining the catalytic behavior. The cleavage of both C–H and C–C bonds involves active oxygen, which can be effectively provided by the reduction of  $Pt^{\delta+}$  to metallic platinum. Thus, the reducibility of  $Pt^{\delta+}$  species, which was calculated by subtraction from the  $Pt^{\delta+}/Pt$  ratio on the oxidized catalyst by that on the reduced catalyst, is considered as a more important factor. Fig. 11 reflects a symmetric relationship between the propane activity and reducibility of metastable  $Pt^{\delta+}$  species. It is seen that more reducible  $Pt^{\delta+}$  sites are formed on 20PtWAl, corresponding to the highest activity for propane oxidation. After then, both of them level off on 30PtWAl.

It has been confirmed using isotopically labeled oxygen experiments that gold-free and gold-doped  $CoO_x$  catalysts oxidize propane to  $CO_2$  via a Mars–Van Krevelen mechanism [37]. It is expected that the total oxidation of propane on Pt/WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts follows a similar reaction route [18]. In this model, the active



Fig. 12. Scheme of propane activation at the platinum-tungsten oxide interface.

oxygen is not the adsorbed one but is provided from the lattice of catalyst. When propane reacts with  $PtO_{\delta/2}$ , propane is oxidized to  $CO_2$  and  $Pt^{\delta+}$  sites are reduced, with molecular oxygen then reoxidizing the catalyst. It has been also pointed out that the availability of appropriate oxygen species and the rate of catalyst reoxidation are crucial in hydrocarbon catalytic combustion over oxide catalysts [38]. In this work, the increased reactivity of platinum on the  $WO_x/Al_2O_3$  support is more likely ascribed to the higher reducibility and especially faster reoxidation ability of Pt species, which can be related to their interactions with the adjacent  $WO_x$  clusters.

#### 4.3. Propane oxidation at the metal/support interface

The results from this study allow us to assume a model for propane dissociative adsorption on Pt/WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts although further evidences are required. Fig. 12 presents a schematic representation of a model involving the initial C-H bond activation at the electronegative sites. The interaction between platinum and the adjacent  $WO_x$  clusters keeps the metal in more electron deficient state. Hereby, metastable  $Pt^{\delta+}$  species, which do not equal to stably oxidized Pt species such as PtO and PtO<sub>2</sub>, are generated. The dissociative adsorption of propane has been presented as the rate-determining step for propane oxidation [39]. Over the WO<sub>x</sub>-modified platinum catalyst, the electropositive hydrogen radical is preferably adsorbed on the W=O bond, while the electronegative propyl radical is adsorbed on the oxidized  $Pt^{\delta^+}$  sites, accompanied with the broken of Pt-O=W bond. Subsequently, the cleavage of C-H bond occurs with the adsorption and activation of gaseous oxygen on Pt sites. With the formation of surface oxygenated complexes (SOCs), the partially oxidized Pt sites are reduced. Simultaneously, the W=O bond is regenerated via a dehydration route.

# 5. Conclusions

From all the above results, the following conclusions can be drawn:

- (1) The temperatures of  $Pt/Al_2O_3$  catalyst for 10% and 50% propane conversion can be lowered with  $WO_x$  modification by about 40 and 80 °C, respectively. The promotion effect of the acidic additives is limited when the loading amount of  $WO_3$  exceeds 20 wt.% of the alumina support.
- (2) The large different activities of Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, despite their similar platinum dispersion, is ascribed to the improved reducibility of metastable Pt<sup> $\delta$ +</sup> species by interaction with WO<sub>x</sub> clusters. The accelerated dissociative adsorption of propane on metastable Pt<sup> $\delta$ +</sup> sites via abstraction of H by the adjacent WO<sub>x</sub> appears to be the determining factor of propane oxidation.

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