



FULL PAPERS

Better with tungsten: The 5 wt.% tungsten-modified Pt/ZSM-5 catalyst has better catalytic activity and stability than the Pt/ZSM-5 catalyst in the total oxidation of propane.



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High Performance and Stability of the Pt-W/ZSM-5 Catalyst for the Total Oxidation of Propane: The Role of **Tungsten**

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Tungsten-modified 1.5 wt.% platinum supported on ZSM-5 catalysts were prepared, and their performances for the total oxidation of propane and the role of tungsten in the catalysts were investigated. The results show that the addition of tungsten can improve the catalytic activity of Pt/ZSM-5. When the tungsten loading is 5 wt.%, the Pt-5W/ZSM-5 catalyst demonstrates excellent catalytic activity and its turnover frequency is more than 1 order of magnitude higher than that of the Pt/ ZSM-5 catalyst. Analyses of the surface properties of catalysts reveal that metallic platinum is scarcely found on the Pt/ZSM-5 catalyst without tungsten; the addition of tungsten can modify the nature of platinum species, which results in the presence of metallic platinum in the Pt-W/ZSM-5 catalyst. The amount of metallic platinum in the Pt-W/ZSM-5 catalyst depends on the tungsten loading and can correlate directly with its catalytic activity. Therefore, the oxidation resistance of platinum in the Pt-W/ZSM-5 catalyst seems to be responsible for the improved catalytic activity in propane oxidation. In addition, the Pt-5W/ ZSM-5 catalyst demonstrates higher stability; no deactivation of the Pt-W/ZSM-5 catalyst is observed after the online test for 50 h, with the temperature alternating between 200 °C for 10 h and 500 °C for 10 h. Therefore, the Pt-5W/ZSM-5 catalyst demonstrates better catalytic activity for propane oxidation than the Pt/ZSM-5 catalyst after online aging at 700 °C for 30 h.

Introduction

In recent years, the environmental legislation has imposed increasingly stringent targets for permitted levels of atmospheric emission. The emission of volatile organic compounds (VOCs) has received significant attention, owing to an increase in photochemical smog,^[1] depletion of atmospheric ozone,^[2] and production of ground-level ozone.^[3] Of the most prevalent VOCs emissions, the release of light alkanes to the atmosphere has increasingly attracted attention worldwide because its amount released to the atmosphere is continuously increasing as a result of the increasing use of liquefied petroleum gas (primarily composed of propane and butane) and compressed natural gas (methane) as substitutes in the gasoline and diesel vehicles. Light alkanes are the largest fraction of hydrocarbons (HCs) in automobile exhausts and can be removed with great difficulty from these emissions. Moreover, the amount of light alkanes released from the stationary sources is increasing with the development of chemical processes and products. Hence, it is important to control the emissions of light alkanes for a wide range of applications. Catalytic oxidation has been identified as one of the most efficient ways to control the

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emission of light alkanes because of its lower combustion temperature and no supplementary fuel.^[4] Of the light alkanes, propane is difficult to be destroyed^[5,6] and hence it is often used as a model gas. For propane oxidation, metal oxides, particularly cobalt oxide, have been used as catalysts because they demonstrate better catalytic activity.^[7,8] However, they easily lose their catalytic activities, owing to particle aggregation at high temperatures. The noble metal catalysts of platinum and palladium possess higher catalytic activity and thermal stability for the total oxidation of propane.^[9-13] Compared with the supported palladium catalysts, the supported platinum catalysts are found to be the most effective for the catalytic total oxidation of propane.^[14]

The total oxidation of propane over platinum catalysts supported on MgO, Al₂O₃, SiO₂-Al₂O₃, zeolite, and TiO₂-SiO₂ has been studied.^[15-18] The platinum catalyst on the strong acidic support showed higher activity than that on the weaker acidic support, because the surface acidity of the support affected the oxidation state of platinum.^[15, 16, 19, 20] Owing to its excellent thermal stability, strong acidity, unique pore structure, and larger surface area, [21] ZSM-5 zeolite has been widely used as the catalytic support material for various catalytic reactions, such as Fischer-Tropsch synthesis,^[22] N₂O decomposition,^[23] reduction of NO_x by CO,^[24] total oxidation of propane, and adsorption of HCs under cold start.^[25-27]

ZSM-5 zeolite has high HC_x trapping capacity,^[28,29] and the platinum catalyst supported on ZSM-5 has excellent catalytic activity for propane oxidation than does the Pt/Al₂O₃ cata-



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ChemCatChem 0000, 00, 1 – 10 These are not the final page numbers! **77**

lyst.^[30, 31] However, the light-off temperature of HC_x over the Pt/ ZSM-5 catalyst is always higher than the desorption temperature of HC_x adsorbed, which means that most of HC_x has been desorbed before reaching the active temperature of HC_x over the catalyst. Thus, the efficiency of HC emission elimination is relatively low during the cold start. Therefore, to effectively reduce HC emission, it is necessary to design and prepare a catalyst with a low light-off temperature and low total conversion temperature for propane oxidation. The research results showed that the catalytic activity of Pt/Al₂O₃ for propane combustion can be improved by adding electrophilic additives (e.g., W, Mo, and V) to the Al₂O₃ support.^[20,32] However, the studies on the modification of the platinum catalyst supported on ZSM-5 are scarcely reported.

Herein, we attempt to modify the Pt/ZSM-5 catalyst with tungsten oxide to develop a more efficient catalyst for propane oxidation. The results show that tungsten-modified Pt/ZSM-5 catalysts demonstrate better catalytic activity and stability than the Pt/ZSM-5 catalyst without tungsten. On the basis of the physicochemical properties of the tungsten-modified Pt/ZSM-5 catalyst investigated by using XRD, laser Raman spectroscopy, hydrogen-temperature-programmed reduction (TPR), temperature-programmed desorption of ammonia (NH₃-TPD), and X-ray photoelectron spectroscopy (XPS), here we discuss the effect of tungsten on the improved catalytic activity.

Results and Discussion

Effect of tungsten on the catalytic activity of the Pt/ZSM-5 catalyst for propane oxidation

The catalytic oxidation of propane over Pt/ZSM-5 catalysts with different tungsten loadings is shown in Figure 1. The temperatures for 10, 50, and 90% propane conversion (denoted as T_{10} , T_{50} , and T_{90}) are shown in Table 1. The CO₂ product is observed only during the catalytic oxidation of propane. The results show that the catalytic activity of the Pt/ZSM-5 catalyst for propane oxidation is improved significantly by a modification in tungsten loading, thus, the tungsten loading affects the catalytic activity of the Pt/ZSM-5 catalyst.



Figure 1. Propane catalytic oxidation over the Pt-W/ZSM-5 catalyst with different tungsten loadings.

Table 1. $T_{10'}$, $T_{50'}$, $T_{90'}$, reaction rates, and turnover frequencies (TOFs) of Pt-W/ZSM-5 catalysts.						
Catalyst	Cataly T ₁₀	ytic activ T ₅₀	ity [°C] <i>T</i> 90	$r^{[a]}$ [10 ⁻⁷ mol X = catalyst	$g_{x}^{-1}s^{-1}]$ X = Pt	TOF ^[a] [10 ⁻³ s ⁻¹]
Pt/ZSM-5 Pt-1W/ZSM-5 Pt-3W/ZSM-5 Pt-5W/ZSM-5 Pt-7W/ZSM-5	211 196 196 184 193	220 205 203 190 199	240 212 208 195 205	0.26 1.08 1.29 6.83 4.77	21.7 90.0 117 621 434	4.0 17.1 25.4 141 107
[a] Reaction temperature is 200 °C.						

When the tungsten loading is ≤ 5 wt.%, the catalytic activity (as T_{50} and T_{90}) of the Pt-W/ZSM-5 catalyst increases with an increase in tungsten loading. The Pt-5W/ZSM-5 catalyst with 5 wt.% tungsten loading demonstrates the highest catalytic activity, that is, the lowest T_{50} (≈ 190 °C) and T_{90} (≈ 195 °C). Its catalytic activity decreases (T_{50} and T_{90} increase) with an increase in tungsten loading. The Pt-7W/ZSM-5 catalyst demonstrates higher catalytic activity (slightly lower T_{50} and T_{90}) for propane deep oxidation than the Pt-3W/ZSM-5 catalyst.

The catalytic activities of $1.5 \text{ wt.}\% \text{Pt/WO}_x$ and 5 wt.% W/ZSM-5 catalysts for propane oxidation are much lower than those of Pt/ZSM-5 and Pt-5W/ZSM-5 catalysts. The low catalytic activity of the Pt/WO₃ catalyst should be attributed to the low surface area of WO₃, and the low activity of the 5W/ZSM-5 catalyst should be attributed to the low catalytic activity of WO₃ for propane oxidation.

The results in Table 1 show that tungsten-modified Pt/ZSM-5 catalysts have higher reaction rate and turnover frequency (TOF) for propane deep oxidation at 200 °C than the Pt/ZSM-5 catalyst. The reaction rates and TOF values for Pt-5W/ZSM-5 and Pt-7W/ZSM-5 catalysts at 200 °C are more than 1 order of magnitude higher than those for the Pt/ZSM-5 catalyst; for instance, the reaction rate and TOF for the Pt-5W/ZSM-5 catalyst reach $620.9 \times 10^{-7} \text{ mol g}_{Pt}^{-1} \text{ s}^{-1}$ and 0.141 s^{-1} , respectively. Only $21.7 \times 10^{-7} \text{ mol g}_{Pt}^{-1} \text{ s}^{-1}$ and 0.004 s^{-1} are obtained for the Pt/ZSM-5 catalyst. These results show that the presence of tungsten improves the catalytic activity of the Pt/ZSM-5 catalyst for propane deep oxidation.

Stability of the Pt-5W/ZSM-5 catalyst

The catalytic activities of Pt/ZSM-5 and Pt-5W/ZSM-5 catalysts at different reaction temperatures are tested, and the results are illustrated in Figure 2. No deactivation can be observed for Pt/ZSM-5 and Pt-5W/ZSM-5 catalysts after the reaction at 220 and 200 °C for 50 h, respectively. The propane conversion over the Pt-5W/ZSM-5 catalyst at 200 °C reaches approximately 92%, and the propane conversion over the Pt/ZSM-5 catalyst at 220 °C. After it is tested online for 50 h with temperature alternating between 200 °C (220 °C) for 10 h and 500 °C for 10 h over the Pt-5W/ZSM-5 (or Pt/ZSM-5) catalyst, propane conversion does not decrease. These results indicate that both Pt/ZSM-5 and Pt-5W/ZSM-5 catalysts demonstrate excellent stability below 500 °C and that the Pt-5W/

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Figure 2. Propane catalytic oxidation over Pt-5W/ZSM-5 (Pt/ZSM-5) catalysts at 200 $^{\circ}$ C (220 $^{\circ}$ C) with temperature alternating between 200 $^{\circ}$ C (220 $^{\circ}$ C) and 500 $^{\circ}$ C.

ZSM-5 catalyst demonstrates higher propane conversion than the Pt/ZSM-5 catalyst.

To further examine the thermal stability of the Pt-W/ZSM-5 catalyst at a higher temperature, an accelerated aging process was used for Pt/ZSM-5 and Pt-5W/ZSM-5 catalysts, which were calcined online at 700 °C for 30 h; the results are illustrated in Figure 3. After the catalysts are aged at 700 °C for 30 h, the catalytic activity of the Pt/ZSM-5 catalyst scarcely changes and that of the Pt-5W/ZSM-5 catalyst decreases slightly, that is, its T_{90} increases from 204 to 212 °C but is still much lower than T_{90} (254 °C) of the Pt/ZSM-5 catalyst. These results show that the



Figure 3. Propane catalytic oxidation over Pt/ZSM-5 and Pt-5W/ZSM-5 catalysts before and after aging at 700 $^\circ$ C for 30 h.

addition of tungsten to the Pt/ZSM-5 catalyst not only can increase its catalytic activity for propane conversion but can also improve its thermal stability.

Catalyst characterization

The results in Table 2 show that the BET surface areas of Pt-W/ ZSM-5 catalysts decrease with an increase in tungsten loading. The BET surface area of the Pt-7W/ZSM-5 catalyst is only 208 m²g⁻¹ and much lower than that (281 m²g⁻¹) of the Pt/ ZSM-5 catalyst, which can be attributed to the filling of the

Table 2. Chemical compositions, BET surface areas (S_{BET}), and platinum dispersions (D_{Pt}) of Pt-W/ZSM-5 catalysts.							
Catalyst	S_{BET}	Pt in solid ^[a]	W in gel	CO pulse	D _{Pt} ^[b]		
	[m ² g ⁻¹]	[%]	[%]	[µmolg _{cat} ⁻¹]	[%]		
Pt/ZSM-5	281	1.2	0	6.5	10.7		
Pt-1W/ZSM-5	264	1.2	1.0	6.3	10.3		
Pt-3W/ZSM-5	249	1.1	3.0	5.1	9.0		
Pt-5W/ZSM-5	220	1.1	5.0	4.8	8.6		
Pt-7W/ZSM-5	208	1.1	7.0	4.4	7.9		
[a] Platinum content was determined from inductively coupled plasma analysis; [b] platinum dispersion was determined from CO chemisorption measurements and $Pt/CO = 1$.							

pores of the ZSM-5 support by tungsten species. As the surface area of Pt/ZSM-5 reduces because of the presence of tungsten, the platinum dispersion determined by CO chemisorption measurements also decreases. For instance, the dispersion of platinum on the Pt/ZSM-5 catalyst without tungsten is approximately 11% and that on the Pt-7W/ZSM-5 catalyst is only approximately 8%.

The XRD patterns of Pt-W/ZSM-5, W/ZSM-5, and WO₃ are shown in Figure 4. The results show that the diffraction peaks of ZSM-5 can be observed in all Pt-W/ZSM-5 catalysts and no diffraction peaks of W-containing crystalline phases or platinum species are identified, which is due to the low amount and high dispersion of platinum or tungsten over the ZSM-5 support.



Figure 4. Powder XRD patterns of Pt-W/ZSM-5 catalysts.

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Figure 5. Raman spectra of W/ZSM-5 and Pt-W/ZSM-5 catalysts.

To further investigate the status of tungsten species, Pt-W/ ZSM-5 catalysts were characterized by laser Raman spectroscopy, and the results are illustrated in Figure 5. Three main Raman vibration bands centered at 808, 714, and 272 cm⁻¹, which are assigned to polymeric tungsten oxide species,^[33] can be observed for Pt-W/ZSM-5 catalysts with >3 wt.% tungsten loading. The bands at 806 and 712 cm⁻¹ are assigned to the W–O stretching mode (A_{1a}) and W–O bending mode (E_a) , respectively. The band at 271 cm⁻¹ is assigned to the W–O–W bending modes (F_{2a}) of the bridging oxygen.^[34] With an increase in tungsten loading, the Raman vibration bands for polymeric WO₃ crystallites enhance significantly. With an increase in tungsten loading in the Pt/ZSM-5 catalyst to 7 wt.%, the Raman characteristic peaks of polymeric WO₃ crystallites enhance and the shape is similar to the Raman spectrum of bulk WO₃. This implies that a congregation of polytungstate species to large bulk-like crystallites has occurred. The WO₃ surface densities reach 4.5-9.0 W atom nm⁻² to crystallize WO₃ and above 9.0 W atom nm⁻² to crystallize large bulk-like crystallites.^[35] In Pt-W/ZSM-5 catalysts, the tungsten loading is much lower than 4.5 W atom nm⁻². Hence, tungsten oxide on the ZSM-5 support is transformed only to polytungstate species after calcination, which is also observed by Xue et al.^[36] The Raman band centered at approximately 380 cm⁻¹ is assigned to the bending vibration of the W-O bond presented in tungstates.

As shown in Figure 5, the Raman vibration intensities of WO₃ crystallites in the Pt-5W/ZSM-5 catalyst are weaker compared to the Raman bands corresponding to polymeric tungsten oxide species of the 5W/ZSM-5 catalyst without platinum. This indicates that the presence of platinum in W/ZSM-5 can reduce the aggregation of polymeric tungsten oxide species and improve the dispersion of tungsten oxide species on the Pt-W/ZSM-5 catalyst. Notably, the Raman peaks of 5W/ZSM-5 at 714 and 808 cm⁻¹ shift to lower wave numbers (6–10 cm⁻¹) compared to the Pt-5W/ZSM-5 catalyst. The Pt-W/ZSM-5 catalyst demonstrate similar Raman features of WO₃ crystallites. These results confirm the presence of a strong interaction between platinum and tungsten, which leads to the migration of charge density between tungsten and platinum.

The TPR profiles of all catalysts are shown in Figure 6. In the TPR curve of the 5W/ZSM-5 catalyst (Figure 6a), a reduction



Figure 6. Temperature-programmed reduction profiles of W/ZSM-5 and Pt-W/ZSM-5 catalysts.

peak exists at approximately 700 °C, which is related to the reduction of W⁶⁺ to W⁴⁺.^[12,37] For Pt-W/ZSM-5 catalysts, the peak attributed to the reduction of tungsten surface species shifts to a slightly lower temperature, which means that the presence of platinum promotes the reduction of tungsten species significantly. Furthermore, with an increase in tungsten loading in Pt-W/ZSM-5 catalysts, the reduction peak area (i.e., the hydrogen consumption) increases, which demonstrates an increase in reducible tungsten species, along with the reduction temperature. In the TPR curve of the Pt-7W/ZSM-5 catalyst, a higher-temperature reduction peak is observed, which is not presented in other catalysts. This reduction peak is attributed to the reduction of the large bulk-like WO3 crystallites, because pure bulk WO3 crystallites and Pt/WO3 catalysts also demonstrate more than one reduction peak above 600 °C (Figure 6b). The results illustrated in Figure 5 also indicate that the Pt-7W/ ZSM-5 catalyst demonstrates Raman bands of polymeric WO₃ such as pure WO₃ crystallites.

For the reduction peak at approximately 325 °C, its peak area and top temperature increase with an increase in tungsten loading, which is similar to the reduction peak of the 1.5 wt.% Pt/WO₃ catalyst at 387 °C (Figure 6 b). To clarify the reduction peak at 325 °C, the Pt-5W/ZSM-5 catalyst before and after reduction with 5 % H_2/N_2 at 200 °C has been tested by using XPS. The XPS results show that all platinum is presented as metallic platinum (see Figure 8 b), and the tungsten 4f XPS spectra are scarcely changed after reduction at 200 °C for 1 h (see Figure 9). No reduction peak below 500 °C can be ob-

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served in the TPR curve of WO₃ (Figure 6 b). Therefore, the reduction peak at approximately 325 °C is attributed to the reduction of surface tungsten oxide species by hydrogen spillover to WO₃, which was activated by metallic platinum reduced at lower temperature.

The XPS spectra of Pt/ZSM-5, Pt-W/ZSM-5, and W/ZSM-5 catalysts are shown in Figures 7–9, respectively. The results in Figure 7 show that the Pt4f XPS spectra of Pt/ZSM-5 catalysts are overlapped strongly with the Al 2p signal of the ZSM-5



Figure 7. Al 2p and Pt4f of X-ray photoelectron spectroscopy spectra of a) ZSM-5 and b) Pt/ZSM-5. c) The result of spectrum b subtracted from spectrum a.

support; hence, the Al 2p spectrum of ZSM-5 should be subtracted from the XPS spectra of Pt/ZSM-5 and Pt-W/ZSM-5 catalysts. For instance, the Al 2p spectrum (Figure 7a) of ZSM-5 is subtracted from the XPS spectrum (Figure 7b) of Pt/ZSM-5 to obtain the Pt4f spectrum (Figure 7c) of Pt/ZSM-5. The Pt4f XPS spectra of Pt-W/ZSM-5 catalysts shown in Figure 8 result from the XPS spectra of Pt-W/ZSM-5 catalysts upon subtracting the Al 2p spectrum (Figure 7a) of ZSM-5.

The peaks of Pt4f are generally observed as a pair, and the binding energy (BE) of Pt4f_{5/2} peak is approximately 3.3 eV higher than that of $Pt4f_{7/2}$. The BEs of $Pt4f_{7/2}$ peaks for Pt^0 , Pt²⁺, and Pt⁴⁺ ions are 71.5, 72.4, and 74.5 eV, respectively,^[10,38] which indicate an increase in the BE of platinum with an increase in the oxidation state of platinum. As shown in Figure 8a, the BEs of $Pt4f_{7/2}$ and $Pt4f_{5/2}$ peaks of Pt/ZSM-5 are strongly affected by tungsten loading. For the Pt/ZSM-5 catalyst without tungsten, the peaks of $Pt4f_{7/2}$ are observed at 72.8 and 74.6 eV, which is attributed to PtO and PtO₂, respectively,^[4] in which the intensity ratio of Pt^{2+} and Pt^{4+} is approximately 45:55. For Pt-W/ZSM-5 catalysts, the peaks of Pt⁰, Pt²⁺, and Pt⁴⁺ are observed by curve fitting of Pt4f doublet peaks with the following restrictions: the doublet separation is set to 3.3 eV for all three platinum species and the area ratio of $4\,f_{7/2}$ and 4f_{5/2} was set to 4:3^[39]; the results are illustrated in Figure 8a, and the surface compositions of Pt-W/ZSM-5 catalysts determined from XPS data are listed in Table 3. The results show that the peaks of Pt4f_{7/2} shift to lower BEs and that the peak at approximately 71.5 eV corresponds to metallic platinum (Pt⁰). With an increase in tungsten loading, the platinum

surface concentration in the Pt-W/ZSM-5 catalyst decreases slightly, owing to an increase in tungsten surface concentration, in which the surface concentration of Pt^0 increases



Figure 8. Pt4f XPS spectra of Pt-W/ZSM-5 (A) and reduced Pt-5W/ZSM-5 (B) and Pt/ZSM-5 (C) at 100 or 200 $^{\circ}$ C by 5 $^{\circ}$ H₂/N₂.

Table 3. Surface element concentrations of Pt-W/ZSM-5 catalysts determined by fitting the XPS data.							
Catalyst	Pt	Pt ⁰ /PtO/PtO ₂	W	O ^[a]			
	[%]	[%]	[%]	[%]			
Pt/ZSM-5	0.56	-/44.8/55.2	-	-			
Pt-1W/ZSM-5	0.54	8.8/51.2/39.9	0.68 (35.71) ^[b]	9.9 (531.5)			
Pt-3W/ZSM-5	0.53	17.3/58.2/24.5	1.24 (35.82)	9.7 (531.4)			
Pt-5W/ZSM-5	0.52	18.6/59.1/22.3	1.79 (35.93)	9.4 (531.1)			
Pt-7W/ZSM-5	0.48	17.8/60.5/21.6	1.83 (35.83)	9.2 (530.9)			
[a] Relative concentration of oxygen species in tungsten oxide was determined by fitting the XPS data. XPS=X-ray photoelectron spectroscopy;[b] The values in parentheses are peak binding energy (in eV).							

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Figure 9. W4f X-ray photoelectron spectroscopy spectra of A) Pt-W/ZSM-5 and B) reduced Pt-5W/ZSM-5 with 5% H_2/N_2 at 100 and 200 °C.

(except the Pt-5W/ZSM-5 catalyst), but those of PtO and PtO_2 decrease. Of the Pt-W/ZSM-5 catalysts, the Pt-5W/ZSM-5 catalyst has the highest surface concentration of Pt^0 .

The W4f XPS spectra of Pt-W/ZSM-5 catalysts are shown in Figure 9. All samples present two peaks, and the W4f_{7/2} peaks are located at 35.7–36 eV, which are ascribed to the presence of W^{6+} ions.^[40,41] In addition, the W4f_{7/2} peak shifts to a higher BE with an increase in tungsten loading, in which the BE of the W4f_{7/2} peak of the Pt-5W/ZSM-5 catalyst is the highest (36 eV).

The O 1s XPS spectra of Pt-W/ZSM-5 catalysts are shown in Figure 10. For the Pt/ZSM-5 catalyst, its O 1s peak at approxi-



Figure 10. O1s X-ray photoelectron spectroscopy spectra of Pt-W/ZSM-5 catalysts.

mately 532.8 eV is fitted only to one peak (or unfitted), which is assigned to the lattice oxygen species of the support.^[36] For the Pt-W/ZSM-5 catalyst, an additional small peak exists at approximately 531 eV, which can be attributed to the oxygen species in tungsten oxide. The BE and relative concentration of oxygen for Pt-W/ZSM-5 catalysts are listed in Table 3, and they decrease with an increase in tungsten loading.

Discussion

The catalytic activities of supported Pt-based catalysts are affected by pretreatment conditions, support kinds, and promoters.^[17,30,42-45] However, the studies of Pt/ZSM-5 catalysts modified with other heteroatoms for propane oxidation are scarcely reported. The aforementioned results show that the catalytic activity of the Pt/ZSM-5 catalyst for propane oxidation can be improved by adding tungsten oxide. The TOF of the Pt/ZSM-5 catalyst at 200 $^{\circ}$ C is only 0.004 s⁻¹; however, for the Pt-5W/ ZSM-5 catalyst with 5 wt.% tungsten loading, the TOF at 200 °C reaches 0.140 s⁻¹, which is much higher than that of Pt/ Al_2O_3 (0.023 s⁻¹) and Pt/MgO (0.0083 s⁻¹) catalysts at 260 °C.^[30] After the Pt-5W/ZSM-5 catalyst is aged at 700 °C for 30 h, it still demonstrates higher catalytic activity for propane deep oxidation compared to the Pt/ZSM-5 catalyst. Thus, it is important to clarify the role of tungsten species in improving the catalytic activity of the W-modified Pt/ZSM-5 catalyst.

Metal dispersion is one of the factors that affect the catalytic activity of supported metal catalysts. Kobayashi et al. reported that the catalytic activity of platinum supported on a TiO₂based carrier for propane combustion was improved with a decrease in platinum dispersion.^[4] No direct correlation between dispersion and catalytic activity is evident from Tables 1 and 2. Although platinum dispersion decreases with an increase in tungsten loading, which is also observed in the XPS spectra, the catalyst with 7 wt.% tungsten demonstrates a catalytic activity lower than that of the catalyst with 5 wt.% W. Thus, the variation in the catalytic activity after adding tungsten to Pt/ ZSM-5 catalysts is not dependent on platinum dispersion. The results in Figure 1 show that the 5W/ZSM-5 catalyst without platinum demonstrates a relatively lower activity for propane oxidation. Hence, the improvement in the catalytic activity of Pt-W/ZSM-5 cannot be attributed to the direct catalysis of tungsten oxide.

The results of Raman spectra (Figure 5) and TPR testing (Figure 6) show that platinum in Pt-W/ZSM-5 catalysts can inhibit the aggregation of tungsten species and enhance the reducibility of tungsten species, that is, tungsten species can be reduced at lower temperature, whereas adding tungsten to Pt/ZSM-5 catalysts can significantly affect the oxidation state of platinum. The surface platinum species on the Pt/ZSM-5 catalyst are completely oxidized, and no metallic platinum (Pt⁰) is observed in its XPS spectrum. However, in the XPS spectra of Pt-W/ZSM-5 catalysts (Figure 8), the peak of metallic platinum can be observed because of the addition of tungsten and the relative surface concentration of Pt⁰ increases with an increase in tungsten loading to \leq 5 wt.%. With an increase in tungsten loading to 7 wt.%, the surface Pt⁰ concentration decreases

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slightly (Table 3); the maximum concentration of Pt^0 can be obtained on the Pt-5W/ZSM-5 catalyst.

The reaction rates and TOFs are plotted against the relative surface concentrations of Pt^0 over Pt-W/ZSM-5 catalysts in Figure 11. The reaction rates over Pt-W/ZSM-5 catalysts are found to be homologously correlated with the surface concentration of Pt^0 . The higher the surface concentration of Pt^0 , the



Figure 11. Influence of the relative surface concentration of Pt⁰ over the Pt-W/ZSM-5 catalyst on the reaction rate and TOF.

higher the reaction rate. The oxidation state of platinum affects the catalytic activity of the Pt-W/ZSM-5 catalyst for propane oxidation, and platinum oxide in the presence of metallic platinum demonstrates high catalytic activity for propane oxidation.^[20] Thus, platinum oxide in the presence of metallic platinum is responsible for high catalytic activity of the Pt-W/ZSM-5 catalyst for propane oxidation and its catalytic activity is related to the surface concentration of Pt⁰.

Yazawa et al. reported that the acid strength of the support materials has a larger effect on the catalytic activity of the platinum-supported catalyst for propane combustion than does the dispersion of platinum and that the catalytic activity of the platinum-supported catalyst can be improved with more acidic support materials.^[15] The TPD of NH₃ adsorbed on Pt-W/ZSM-5 catalysts has been investigated, and the results are illustrated in Figure 12. The results show that the tungsten loading in the Pt/ZSM-5 catalyst scarcely affects their NH₃-TPD curves, that is,



Figure 12. TPD curves of NH₃ adsorbed on Pt-W/ZSM-5 catalysts.

the addition of tungsten to the Pt/ZSM-5 catalyst scarcely varies its acidic properties, because ZSM-5 is a strong acidic material.

The aforementioned results (Figure 9 and Table 3) show that the W4f_{7/2} signal shifts to a higher BE with an increase in tungsten loading to \leq 5 wt.% in Pt-W/ZSM-5 catalysts but the BE of W4f_{7/2} of the Pt-7W/ZSM-5 catalyst is the same as that of the Pt-3W/ZSM-5 catalyst. In general, the shift in BE suggests a variation in the electronic state or lattice strain. The Pt-5W/ZSM-5 catalyst has the highest BE (35.93 eV) of W4f_{7/2} among all Pt-W/ZSM-5 catalysts, which indicates the presence of tungsten with the highest (e.g., >6+) oxidation state. When the relative concentration of metallic platinum and the BE changes of $W4f_{7/2}$ are taken into account, it is clear that as an electron donor tungsten species lose electrons that are transferred to platinum species, resulting in an increase in the electron density of platinum species to form metallic platinum, which has been completed by an electron transfer from tungsten to platinum at the W-Pt interface based on the interaction between platinum and tungsten oxide. Hence, more metallic platinum and the shift of the $W4f_{7/2}$ signal to higher BE are observed over W-modified Pt/ZSM-5 catalysts. The more the shift of the W4f_{7/2} signal to higher BE, the more the metallic platinum located in the catalyst. Therefore, the most metallic platinum exists in the Pt-5W/ZSM-5 catalyst. With an increase in tungsten loading to 7 wt.% (Pt-7W/ZSM-5), large bulk-like WO3 species form (Raman spectra in Figure 5 and TPR curves in Figure 6), which results in the BE of $W4f_{7/2}$ of the Pt-7W/ZSM-5 catalyst shifting to a lower value compared to the Pt-5W/ZSM-5 catalyst because of a variation in the lattice strain of tungsten oxides. Hence, the presence of bulk-like WO₃ species in the Pt-7W/ZSM-5 catalyst weakens the interaction between platinum and tungsten oxide, which results in a decrease in the surface metallic platinum concentration (i.e., the oxidation resistance of platinum) and catalytic activity for propane oxidation.

Conclusions

In summary, the catalytic activity of the 1.5 wt.%Pt/ZSM-5 catalyst for propane oxidation has been improved by adding

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tungsten. With 5 wt.% tungsten loading, a highly effective catalytic activity of the Pt-W/ZSM-5 catalyst can be obtained and its TOF is more than 1 order of magnitude higher than that of the Pt/ZSM-5 catalyst. The improvement in the catalytic activity of the Pt-W/ZSM-5 catalyst should be related to the interaction between platinum and tungsten. The presence of tungsten can result in the presence of metallic platinum in Pt-W/ZSM-5 catalysts, and metallic platinum is scarcely found on the Pt/ ZSM-5 catalyst without tungsten. Therefore, the addition of tungsten to Pt/ZSM-5 catalysts can increase the oxidation resistance of platinum by an electron transfer from tungsten to platinum at the W-Pt interface based on the interaction between platinum and tungsten oxide, which is responsible for the improvement in the catalytic activity. In addition, the presence of platinum reduces the aggregation of tungsten oxides and improves the reducibility of tungsten oxides.

The Pt-5W/ZSM-5 catalyst also demonstrates excellent stability. No decrease in catalytic activity can be observed after the online test for 50 h with temperature alternating between 200 °C for 10 h and 500 °C for 10 h; after online aging at 700 °C for 30 h, the Pt-5W/ZSM-5 catalyst still demonstrates better catalytic activity than the Pt/ZSM-5 catalyst.

Experimental Section

Catalyst preparation

Ammonium tungstate hydrate (0.066, 0.195, 0.328, or 0.459 g; Sinopharm Chemical Reagent Co., Ltd., China) and oxalic acid (0.2 g; Sinopharm Chemical Reagent, China) were dissolved in deionized water (40 mL) under stirring. Then, aqueous $Pt(NO_3)_2$ solution (0.598 g, 15.05 wt.%; Heraeus Materials Technology Shanghai Ltd., China) was added to that mixture and the solution was heated to 80 °C under stirring. Next, H-ZSM-5 (6 g; Nankai University Catalyst Co. Ltd.; Si/Al=50; BET surface area=310 m²g⁻¹) was added to the heated solution and the solution was stirred continuously at 80 °C until water had dried up. Finally, the catalysts were dried at 110 °C for 12 h and calcined at 500 °C for 3 h under static air in a muffle furnace. The as-prepared catalysts consisted of 1.5 wt.% Pt and 1.0–7.0 wt.% W, which were labeled as Pt-xW/ZSM-5 (x=1, 3, 5, 7). A similar method was used to prepare 1.5 wt.%Pt/ZSM-5 and 5W/ZSM-5 catalysts.

Catalyst characterization

The surface areas of the catalysts were determined from the N₂ adsorption measurements at -196 °C with a Micromeritics ASAP 2400 instrument by using the BET method. The samples were degassed at 180 °C for 12 h before measurement. The XRD patterns of the catalysts were recorded on a Rigaku D/Max-RC diffractometer using CuK_a radiation ($\lambda = 1.541$ Å) and operating at 40 kV and 40 mA. The laser Raman spectra of the catalysts were recorded on a Renishaw inVia Reflex spectrometer equipped with a charge-coupled device detector. The excitation source used was an Ar ion laser ($\lambda = 514.5$ nm) with a spot size of approximately 1 mm. The power of the incident beam on the catalyst was 3 mW.

The XPS spectra were recorded at 298 K on a Thermo Scientific ES-CALAB 250Xi X-ray photoelectron spectrometer using AlK_{α} radiation (1486.6 eV) and operating at 150 W. All BEs were determined with respect to the C 1s line (284.8 eV) originating from adventi-

tious carbon. The BE of the target elements (Pt4f, W4f, O 1s, and C 1s) was determined at a pass energy of 25 eV. The XPS spectra were fitted with XPS Peak 4.1 software using a properly weighted sum of Lorentzian–Gaussian line shape after background subtraction according to Shirley's method.

The platinum content in the catalyst was measured by using ICP on a Vanan 710 instrument. Platinum dispersion was determined through pulsed CO chemisorption at 35 °C, in which Ar (flow rate 30 mLmin⁻¹) was used as a carrier gas and a pulse of 10.22 vol% CO/Ar (0.5173 mL) was injected. Before CO uptake determination, all samples were pretreated in H₂ (50 mLmin⁻¹) at 400 °C for 2 h and then flushed with Ar (30 mLmin⁻¹) for 30 min. An adsorption stoichiometry of Pt/CO=1 was assumed while determining platinum dispersion.

The TPR of the catalyst was performed in a conventional flow system equipped with a thermal conductivity detector (TCD). The catalyst (100 mg) was used. The reducing gas was consisted of 10 vol% H_2 in Ar, and its flow rate was 45 mLmin⁻¹. The reactor was heated from RT to 800 °C, with a heating rate of 10 °Cmin⁻¹.

TPD of NH₃ adsorbed on the catalyst was performed in a conventional flow system equipped with a TCD. The sample was pretreated in N₂ at 600 °C for 1 h before adsorbing NH₃. The NH₃-TPD experiments were performed at 50–600 °C under N₂ flow (flow rate 30 mLmin⁻¹). The heating rate was 10 °C min⁻¹.

Catalytic activity testing

The catalytic activity of the catalyst was measured in a fixed-bed laboratory microreactor system. The catalyst (200 mg, 40–60 mesh) was placed in a 10 mm quartz reactor tube. The feed gas was consisted of 2000 ppm $C_3H_8+2\%$ O_2/Ar balanced, and its flow rate was 100 mL min⁻¹. The reactants and products were analyzed online by using a GC equipped with a TCD. The catalytic activities were characterized by propane conversion (%), T_{10} , T_{50} , and T_{90} , which are the reaction temperatures for the propane conversion of 10, 50, and 90%, respectively. All carbon balances were calculated and were in the range of $100\pm5\%$. Reaction rates and TOFs were measured in a differential mode with the propane conversion of 5–15% by controlling the W/F ratio. Both external and internal mass transport limitations can be excluded by varying the particle size and W/F ratio (the ratio of catalyst weight to total flow rate). All data were obtained after the reaction stabilizes for 60 min.

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 A. C. Lewis, N. Carslaw, P. J. Marriott, R. M. Kinghorn, P. Morrison, A. L. Lee, K. D. Bartle, M. J. Pilling, *Nature* **2000**, *405*, 778–781.

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CHEMCATCHEM Full papers

- [2] T. Garcia, B. Solsona, D. M. Murphy, K. L. Antcliff, S. H. Taylor, J. Catal. 2005, 229, 1–11.
- [3] B. J. Finlayson-Pitts, J. N. Pittts, Jr., Science 1997, 276, 1045-1051.
- [4] M. Kobayashi, A. Morita, M. Ikeda, Appl. Catal. B 2007, 71, 94-100.
- [5] J. Okal, M. Zawadzki, W. Tylus, Appl. Catal. B 2011, 101, 548-559.
- [6] T. V. Choudhary, S. Banerjee, V. R. Choudhary, Appl. Catal. A 2002, 234, 1–23.
- [7] Q. Liu, L. C. Wang, M. Chen, Y. Cao, H. Y. He, K. N. Fan, J. Catal. 2009, 263, 104–113.
- [8] B. Solsona, T. E. Davies, T. Garcia, I. Vazquez, A. Ddjoz, S. H. Taylor, Appl. Catal. B 2008, 84, 176–184.
- [9] L. Zhang, D. Weng, B. Wang, X. D. Wu, Catal. Commun. 2010, 11, 1229– 1232.
- [10] M. Y. Kim, S. M. Park, G. Seo, K. S. Song, Catal. Lett. 2010, 138, 205-214.
- [11] J. E. Park, K. B. Kim, K. W. Seo, K. S. Song, E. D. Park, *Res. Chem. Intermed.* 2011, *37*, 1135 – 1143.
- [12] M. N. Taylor, W. Zhou, T. Garcia, B. Solsona, A. F. Carley, C. J. Kiely, S. H. Tarlor, J. Catal. 2012, 285, 103–114.
- [13] M. Taylor, E. N. Ndifor, T. Garcia, B. Solsona, A. F. Caley, S. H. Taylor, Appl. Catal. A 2008, 350, 63–70.
- [14] K. Muto, N. Katada, M. Niwa, Appl. Catal. A 1996, 134, 203-215.
- [15] Y. Yazawa, N. Takagi, H. Yoshida, S. I. Komai, A. Satsuma, T. Tanaka, S. Yoshida, T. Hattori, *Appl. Catal. A* 2002, 233, 103 112.
- [16] Y. Yazawa, H. Yosida, T. Hattori, Appl. Catal. A 2002, 237, 139-148.
- [17] K. B. Kim, Y. H. Kim, K. S. Song, E. D. Park, *Rev. Adv. Mater. Sci.* 2011, 28, 35–39.
- [18] M. Y. Kim, J. H. Park, C. H. Shin, S. W. Han, G. Seo, Catal. Lett. 2009, 133, 288–297.
- [19] H. Yoshida, Y. Yazawa, T. Hattori, *Catal. Today* **2003**, *87*, 19–28.
- [20] Y. Yazawa, H. Yoshida, T. Hattori, Appl. Catal. A 2002, 233, 113-124.
- [21] T. Kanazawa, Appl. Catal. B 2006, 65, 185-190.
- [22] S. Bessell, Appl. Catal. A 1995, 126, 235-244.
- [23] B. M. Abu-Zied, W. Schwieger, Appl. Catal. B 2009, 85, 120-130.
- [24] Y. S. Bi, L. Cheng, G. X. Lu, J. Mol. Catal. A 2007, 266, 173-179.
- [25] X. S. Liu, J. K. Lampert, D. A. Arendarskiial, R. J. Farrauto, Appl. Catal. B 2001, 35, 125–136.

- [26] A. K. Neyestanaki, N. Kumar, L. E. Lindfors, Fuel 1995, 74, 690-696.
- [27] N. A. Kalantar, N. Kumar, L. E. Lindfors, Appl. Catal. B 1995, 7, 95-111.
- [28] A. V. Ivanov, G. W. Graham, M. Shelef, *Appl. Catal. B* 1999, *21*, 243–258.
 [29] D. S. Lafyatis, G. P. Ansell, S. C. Bennett, J. C. Frost, P. J. Millington, R. R.
- Rajaram, A. P. Walker, T. H. Ballinger, *Appl. Catal. B* **1998**, *18*, 123–135.
- [30] T. F. Garetto, E. Rincon, C. R. Apesteguia, Appl. Catal. B 2004, 48, 167– 174.
- [31] T. F. Garetto, E. Rincon, C. R. Apesteguia, Appl. Catal. B 2007, 73, 65-72.
- [32] M. S. Avila, C. I. Vignatti, C. R. Apesteguia, V. Venkat Rao, K. Chary, T. F. Garetto, *Catal. Lett.* **2010**, *134*, 118–123.
- [33] Y. Liu, C. Luo, H. C. Liu, Angew. Chem. 2012, 124, 3303-3307; Angew. Chem. Int. Ed. 2012, 51, 3249-3253.
- [34] W. P. Shan, F. D. Liu, H. He, X. Y. Shi, C. B. Zhang, Chem. Commun. 2011, 47, 8046-8048.
- [35] I. E. Wachs, T. Kim, E. I. Ross, Catal. Today 2006, 116, 162-168.
- [36] N. H. Xue, L. Nie, D. M. Fang, X. F. Guo, J. Y. Shen, W. P. Ding, Y. Chen, Appl. Catal. A 2009, 352, 87–94.
- [37] D. C. Vermaire, P. C. Van Berge, J. Catal. 1989, 116, 309-317.
- [38] L. Olsson, E. Fridell, J. Catal. 2002, 210, 340-353.
- [39] A. Lewera, L. Timperman, A. Roguska, N. A. Vante, J. Phys. Chem. C 2011, 115, 20153–20159.
- [40] A. Romanyuk, R. Steiner, P. Oelhafen, J. Biskupek, U. Kaiser, D. Mathys, V. Spassov, J. Phys. Chem. C 2008, 112, 11090-11092.
- [41] B. Šmid, Z. J. Li, A. Dohnalkova, B. W. Arey, R. S. Smith, V. Matolin, B. D. Kay, Z. Dohnalek, J. Phys. Chem. C 2012, 116, 10649–10655.
- [42] C. P. Hubbard, K. Otto, H. S. Gandhi, K. Y. S. Ng, J. Catal. 1993, 139, 268– 276.
- [43] A. Ishikawa, S. Komai, A. Satsuma, T. Hattori, Y. Murakami, Appl. Catal. A 1994, 110, 61–66.
- [44] X. D. Wu, Z. Zhou, D. Weng, B. Wang, J. Environ. Sci. 2012, 24, 458-463.
- [45] J. Volter, G. Lietz, H. Spindler, H. Lieske, J. Catal. 1987, 104, 375-380.

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