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Catalytic Combustion of Propane over Pt-Mo/ZSM-5 Catalyst: The Promotional Effects of Molybdenum

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Abstract: To improve propane combustion activity and illustrate the promotional effects of molybdenum doping, Pt-Mo/ZSM-5 catalysts with different Mo amounts were prepared by the co-impregnation method. XRD, Raman, H₂-TPR, NH₃-TPD, in situ DRIFTs, XPS and other characterizations were performed. The results indicated that the concentration of Pt⁰ in Pt/ZSM-5 catalyst increased after the doping of Mo and the content of Pt⁰ had a positive correlation with the reaction turnover frequency value. The propane combustion activity of Pt/ZSM-5 catalyst was significantly improved after the doping of molybdenum species. Among all the catalysts, Pt-6Mo/ZSM-5 catalyst (Pt/ZSM-5 with 6 wt.% Mo modification) showed the lowest T₅₀ and T₉₀ for propane catalytic combustion. Moreover, the Pt-Mo/ZSM-5 catalyst exhibited outstanding catalytic stability.

Keywords: propane; catalytic combustion; platinum; molybdenum

1. Introduction

The rapid development of industry has brought forward the problem of industrial exhaust emissions [1], of which volatile organic compounds (VOCs) account for a relatively high proportion. The hazard of VOCs should not be underestimated, because it will cause serious harm to human health and destroy the ozone layer [2]. Many countries have issued corresponding laws and regulations to deal with this problem [3]. It is very important to develop VOC treatment technologies. Among all the methods to deal with VOCs, catalytic combustion has many advantages such as low ignition temperature, no secondary pollution and low energy cost [4]. Therefore, it has been widely used in industry [5]. The alkane VOCs represented by propane are stable, which put forward higher requirements for the treatment [6]. The types of catalysts used in the catalytic combustion of propane can be divided into noble metal catalysts and non-noble metal oxides catalysts. Noble metal catalysts include Pt, Pd, Ru, Au and so forth [7–12] while non-noble metal oxides catalysts include Cu, Mn, Ce, Ni oxides and their composite metal oxides [13–17]. Pt is the most active component applied in propane catalytic combustion. However, the Pt-based catalyst is limited by scarce resources. It is particularly valuable to prepare high performance Pt catalysts with low Pt loading. The use of suitable supports and heteroatom doping may help us achieve this goal.

In terms of supports, it was found that the acid sites on the support could enhance the catalytic combustion activity because Pt on more acidic support materials had higher oxidation-resistance [18]. Zeolite is a type of support that can provide strong active sites [19]. At the same time, zeolites also have a large specific surface area and regular pore structures. It was reported that Pt/ZSM-5 catalysts...
had much higher propane combustion activity than Pt/Al$_2$O$_3$ and Pt/MgO [20]. ZSM-5 should be a suitable support for propane catalytic combustion.

The catalytic performance of supported Pt catalysts was also affected by heteroatom doping. Yazawa et al. [21] systematically studied the effects of doping elements on the catalytic performance of Pt/Al$_2$O$_3$ with the molar ratio of doping elements to Pt of 4. They found a positive correlation between the catalytic activity of Pt-based catalysts and the electronegativity of added elements. After doping with electrophilic metal element additives such as V, W, Mo and Nb, Pt was more difficult to be oxidized to a high valence state. Therefore, the doped catalysts exhibited stronger oxidation resistance and better catalytic activity. Avila et al. [22] prepared Pt/V-Al$_2$O$_3$ catalysts with different V doping ratios, and found that the catalyst with 20%V loading amount had the best activity for propane combustion. Moreover, the activity of Pt-V/Al$_2$O$_3$ catalysts was affected by the preparation methods, and the catalyst prepared by the co-impregnation method had a superior propane combustion activity than those of catalysts prepared by other methods, which could be attributed to the good redox property resulted from the interaction between platinum particles and vanadium species [23]. Lu’s Group [24] reported that the doping of tungsten on Pt/ZSM-5 catalysts could increase the content of Pt$^{0}$, which was the key factor of propane combustion. The catalysts with 5% W loading had the highest content of Pt$^{0}$ and exhibited the best catalytic activity as well as enhanced stability. Luo’s Group [25] prepared Pt-Nb/Al$_2$O$_3$ catalysts and found that the doping of Nb could significantly increase the content of Pt$^{0}$. The authors declared that the increase in catalytic combustion activity of propane was the result of the combined effect of Pt$^{0}$ and Pt$^{2+}$.

As mentioned above, Mo is an electrophilic metal element. A low Pt content Pt-Mo/ZSM-5 catalyst, which combines the advantages of ZSM-5 and Mo, could be a good catalyst for the combustion of propane. However, rare research on it can be found currently. Herein, we used ZSM-5 as the support to prepare Pt/ZSM-5 with Pt loading of 1 wt.%, then doped it with different proportions of Mo to obtain Pt-Mo/ZSM-5 catalysts. The propane combustion performance of Pt-Mo/ZSM-5 was investigated. XRD, TEM, BET, H$_2$-TPR, XPS and other characterization methods were taken to study the physical and chemical properties of the catalysts. The promotional effects of Mo doping on the catalyst activity were evaluated.

2. Results and Discussion

2.1. Textural Properties

The X-ray fluorescence (XRF) spectra were applied to investigate the actual compositions of as-prepared catalysts and the results are shown in Table 1. The BET surface areas measured by N$_2$ adsorption (Table 1) decreased in the following order: Pt/ZSM-5 > Pt-2Mo/ZSM-5 > Pt-4Mo/ZSM-5 > Pt-6Mo/ZSM-5 > Pt-8Mo/ZSM-5. The surface area of the Pt/ZSM-5 catalyst was 299.2 m$^2$/g while that of Pt-8Mo/ZSM-5 was 248.0 m$^2$/g. The results indicated that the BET surface area of Pt/ZSM-5 catalyst decreased slightly after molybdenum species loading. This may be due to the pore overlapping of Pt/ZSM-5 by molybdenum species. However, the surface areas of all the tested samples were still relatively large. The variation of pore volumes followed a similar rule. The pore volumes of Pt-Mo/ZSM-5 samples reduced with the increase in doping amount of molybdenum.
Table 1. Textural properties of Pt-Mo/ZSM-5 catalysts with different Mo amounts.

| Sample         | Pt (wt.%) a | Mo (wt.%) a | Dispersion of Pt (%) b | \( S_{BET} \) (m²/g) | Volume of Pores (cm³/g) | \( d_{Pt} \) (nm) c |
|----------------|------------|------------|-----------------------|---------------------|------------------------|---------------------|
| Pt/ZSM-5      | 0.98       | —          | 31.4                  | 299.2               | 0.134                  | 2.75                |
| Pt-2Mo/ZSM-5  | 0.99       | 1.95       | 33.1                  | 283.8               | 0.116                  | 2.50                |
| Pt-4Mo/ZSM-5  | 0.97       | 3.86       | 36.7                  | 266.1               | 0.115                  | 1.91                |
| Pt-6Mo/ZSM-5  | 0.95       | 5.93       | 34.2                  | 265.8               | 0.113                  | 2.15                |
| Pt-8Mo/ZSM-5  | 0.97       | 7.75       | 37.8                  | 248.0               | 0.107                  | 1.82                |

a Element content measured by X-ray fluorescence (XRF). b Dispersion measured by CO-Chemisorption. c Particle size obtained by HRTEM.

Figure 1 shows the XRD patterns of Pt-Mo/ZSM-5 catalysts. It can be observed that all samples exhibited the characteristic diffraction peaks of the MFI structure. After metal loading, the MFI structure of the ZSM-5 support was maintained. No characteristic diffraction peaks of Pt and Mo species were observed. The result indicated that the Pt and Mo species were highly dispersed on ZSM-5 [26]. The good dispersion of metal components also proved that ZSM-5 was a suitable support for uniform metal loading.

Figure 1. X-ray diffraction (XRD) patterns of ZSM-5, 6Mo/ZSM-5 and Pt-Mo/ZSM-5 catalysts with different Mo amounts.

The HRTEM images of the Pt-Mo/ZSM-5 catalysts and the Energy Dispersive Spectrometer (EDS) mapping images of the Pt-6Mo/ZSM-5 catalyst are shown in Figure 2. In the EDS mapping images, it was observed that Pt and Mo were evenly distributed on the ZSM-5 support, which may lead to a certain interaction between Pt and Mo species. Pt and Mo particles were marked on the HRTEM images (Figure 2b), which were determined according to the interplanar spacing of Pt and Mo species (PDF No.04-0802 and PDF No.47-1320). The statistical results of Pt particle size were shown in Figure S1. The average particle size of Pt in the Pt/ZSM-5 catalyst without Mo addition was 2.75 nm, and the range of Pt particle size of the catalysts after doping with Mo was from 1.8 to 2.5 nm (Table 1). The results showed that the size of Pt particles slightly decreased with the addition of Mo. The Pt dispersion measured by CO chemisorption (Table 1) is consistent with the particle size distribution. After the addition of Mo, the dispersion was slightly improved. The dispersion of Pt in Pt/ZSM-5 was 31.4%, while it was from 33.1% to 37.8% in Pt-Mo/ZSM-5.
Raman spectroscopy was performed in order to study the aggregation status of Mo species. Figure 3 showed the Raman spectra of Pt-Mo/ZSM-5, Pt/ZSM-5, bulk MoO_3 and Mo/ZSM-5. All the samples showed similar bands at 290, 340, 660, 820 and 994 cm\(^{-1}\), which were attributed to the typical Raman bands of MoO_3. Concretely, the peaks at 290, 340, 660, 820 and 994 cm\(^{-1}\) were ascribed to bending mode for the double bond (Mo=O) vibration, Mo\(_3\)-O bending mode, triply coordinated oxygen (Mo\(_3\)-O) stretching mode, doubly coordinated oxygen (Mo\(_2\)-O) stretching mode and symmetric O=Mo=O stretching vibration, respectively [27,28].

It was obvious that the peak heights decreased after bulk MoO_3 was distributed on ZSM-5, indicating the aggregation of polymeric molybdenum oxide was reduced [29]. The presence of Pt in Pt-6Mo/ZSM-5 further reduced the peak heights, indicating the dispersion of Mo species on the Pt-Mo/ZSM-5 catalyst was improved. The better dispersion of Mo species on the Pt-Mo/ZSM-5 may due to the interaction between Pt and Mo species.
2.2. Redox and Acid Properties

H$_2$ temperature-programmed reduction (H$_2$-TPR) was conducted to investigate the redox properties of the catalysts. The results of the analyzed samples are displayed in Figure 4a. The TPR curve of all the Pt-Mo/ZSM-5 catalysts showed reduction peaks at 190–230 °C, which could be attributed to the reduction of Pt species [30]. The reduction peak of Pt species in Pt/ZSM-5 was at 230 °C and shifted to a lower temperature after the addition of Mo. Pt-6Mo/ZSM-5 had the lowest reduction temperature at 190 °C. Compared to Pt/ZSM-5, Pt species in Pt-Mo/ZSM-5 catalysts could be more easily reduced. The results suggested that the interaction between Pt and Mo species enhanced the reducibility of the Pt species in catalysts.

The peaks on Pt-Mo/ZSM-5 around 700 °C could be attributed to the reduction of MoO$_3$ [31]. Bulk MoO$_3$ had a reduction peak at 790 °C. This suggested that the existence of Pt would promote the reduction of the molybdenum species [32]. It should be noted that a shoulder peak appeared on the reduction peak of molybdenum species on Pt-8Mo/ZSM-5, indicating that there was an aggregation of polymeric molybdenum oxide species. Extra-wide peaks between 400–550 °C appeared on the pattern of Pt-6Mo/ZSM-5 and Pt-8Mo/ZSM-5 catalysts, which could be attributed to MoO$_3$ clusters with smaller sizes [31] or MoO$_3$ nanoparticles that could be easily reduced [33]. The result further proved that there was an interaction between Pt and Mo species and the interaction affected the redox properties of Pt-Mo/ZSM-5 catalysts.

The acid properties of the catalysts were characterized by NH$_3$-TPD, and the results were shown in Figure 4b. All the curves of the catalysts showed two peaks at 100–200 °C and 300–400 °C, indicating that there are two kinds of acid sites with different strengths. In order to quantitatively compare the amounts of two acid sites in different catalysts, Gaussian integration was performed to obtain the acid content at the strong acid site and the weak acid site (Table 2). The results proved that the introduction of Mo had a negligible effect on the content of strong acid sites. As for the weak acid site, the amount of acid increased obviously with the increase in the Mo doping amount. The weak acid content of Pt/ZSM-5 was 0.16 mmol/g, while the amount of Pt-8Mo/ZSM-5 reached 0.34 mmol/g.

Table 2. Acid properties of Pt-Mo/ZSM-5 catalysts with different Mo amounts.

| Sample      | Weak Acidity (mmol/g) | Strong Acidity (mmol/g) | Total Acidity (mmol/g) |
|-------------|-----------------------|-------------------------|------------------------|
| Pt/ZSM-5    | 0.16                  | 0.13                    | 0.29                   |
| Pt-2Mo/ZSM-5| 0.20                  | 0.14                    | 0.34                   |
| Pt-4Mo/ZSM-5| 0.29                  | 0.14                    | 0.43                   |
| Pt-6Mo/ZSM-5| 0.31                  | 0.15                    | 0.45                   |
| Pt-8Mo/ZSM-5| 0.34                  | 0.13                    | 0.47                   |
2.3. Surface Element Analysis

XPS characterization of Pt and Mo elements was carried out to study the valence of Pt and Mo in the series of catalysts. Figure 5a is the 4f orbit XPS characterization diagram of Pt. The interference of the Al 2p spectrum in ZSM-5 has been deducted from the Pt spectrum (the process of deduction was shown in Figure S2). The peaks of Pt generally appear in pairs, the binding energy (BE) of the Pt4f5/2 peak is about 3.3 eV higher than the BE of the Pt4f7/2 peak, and the area ratio of the two peaks is 4:3 [32]. The 4f XPS of Pt is split according to this peak splitting rule. Pt has three main valence states, among which the binding energies of Pt0, Pt2+ and Pt4+ are 71.5, 72.4 and 74.5 eV, respectively. The FWHM of Pt with different oxidation states is listed in Table S1. The quantitative results of integrating the representative peaks of each valence state are shown in Table 3. The Pt0 content decreased as following order: Pt-6Mo/ZSM-5 > Pt-8Mo/ZSM-5 > Pt-4Mo/ZSM-5 > Pt-2Mo/ZSM-5 > Pt/ZSM-5. After Mo incorporation, the content of Pt0 has been significantly increased. The content of Pt0 in Pt/ZSM-5 is 10.8%, while that of Pt-6Mo/ZSM-5 reached 40.4%. It was proved that the electronic interaction between Pt and Mo caused the change of the valence state of Pt0. The excess Mo amount in Pt-8Mo/ZSM-5 may cause the aggregation of molybdenum oxide species and weaken the interaction between Pt and Mo species. Figure 5b was the 3d orbital XPS representation of Mo. All the Mo doped catalysts showed two peaks whose positions were 232.7–233.0 eV and 236–236.3 eV, which were corresponding to the characteristic peaks of Mo6+ [26]. All the positions of peaks were higher than bulk MoO3 (231.7 eV). In addition, the binding energy of the Pt-Mo/ZSM-5 catalysts shifted to higher BEs compared to the 6Mo/ZSM-5 catalyst, indicating that there was an obvious electronic interaction between Pt and Mo.

![Figure 5](image_url)

**Figure 5.** Pt 4f spectra (a) and Mo 3d spectra (b) of Pt-Mo/ZSM-5 catalysts with different Mo amounts.

**Table 3.** Surface contents of Pt0, Pt2+ and Pt4+ on Pt-Mo/ZSM-5 catalysts measured by XPS.

| Sample         | Pt0 (%) | Pt2+ (%) | Pt4+ (%) |
|----------------|---------|----------|----------|
| Pt/ZSM-5       | 10.8    | 35.9     | 53.3     |
| Pt-2Mo/ZSM-5   | 18.1    | 37.7     | 44.2     |
| Pt-4Mo/ZSM-5   | 22.6    | 33.1     | 44.3     |
| Pt-6Mo/ZSM-5   | 40.4    | 32.8     | 26.8     |
| Pt-8Mo/ZSM-5   | 32.2    | 33.6     | 34.2     |
2.4. Catalytic Tests of Propane Catalytic Combustion

2.4.1. Activity of Propane Catalytic Combustion

Figure 6 showed the catalytic activities of Pt/ZSM-5 catalysts with different Mo amounts for propane combustion. The 6Mo/ZSM-5 sample without Pt showed almost no catalytic activity below 400 °C, indicating that the Mo species and ZSM-5 alone had no direct contribution to the catalytic combustion. The activity of the Pt/ZSM-5 catalysts increased with the increase in Mo loading when the Mo loading is less than 6 wt.%. The order of catalytic activity is: Pt-6Mo/ZSM-5 > Pt-8Mo/ZSM-5 > Pt-4Mo/ZSM-5 > Pt-2Mo/ZSM-5 > Pt/ZSM-5. Table 4 lists the T_{10}, T_{50}, T_{90} (the temperature when the conversion reached 10%, 50%, 90%) and TOF (turnover frequency) of the catalyst at 240 °C. Among the catalysts with different Mo doping amounts, Pt-6Mo/ZSM-5 exhibited the best catalytic activity. The excess loading of Mo had a negative effect on the improvement of catalyst activity. Compared with Pt/ZSM-5 catalyst, Pt-6Mo/ZSM-5 reduced its T_{10}, T_{50} and T_{90} by 50 °C, 40 °C and 40 °C, respectively. It meant that the Pt-6Mo/ZSM-5 could realize the ignition and complete combustion of propane at lower temperatures. The TOF of the catalysts obeyed a similar order: Pt-6Mo/ZSM-5 > Pt-8Mo/ZSM-5 > Pt-4Mo/ZSM-5 > Pt-2Mo/ZSM-5 > Pt/ZSM-5. Mo doping had a significant effect on the TOF of the catalytic combustion reaction. At 240 °C, the TOF value of Pt/ZSM-5 is 79 h^{-1} while it reached 225 h^{-1} in Pt-6Mo/ZSM-5. The TOF value of Pt-6Mo/ZSM-5, markedly enhanced by Mo modification, was almost 3 times that of the Pt/ZSM-5 catalyst.

![Figure 6](image-url)

**Figure 6.** The catalytic activity of Pt-Mo/ZSM-5 catalysts with different Mo amounts and 6Mo/ZSM-5 catalyst for propane combustion.

**Table 4.** The T_{10}, T_{50}, T_{90} and turnover frequency (TOF) values of Pt-Mo/ZSM-5 catalysts with different Mo amounts in propane catalytic combustion reactions.

| Sample          | T_{10} (°C) | T_{50} (°C) | T_{90} (°C) | TOF (h^{-1}) |
|-----------------|-------------|-------------|-------------|--------------|
| Pt/ZSM-5        | 230         | 255         | 295         | 79           |
| Pt-2Mo/ZSM-5    | 210         | 240         | 280         | 126          |
| Pt-4Mo/ZSM-5    | 202         | 228         | 275         | 142          |
| Pt-6Mo/ZSM-5    | 180         | 215         | 255         | 225          |
| Pt-8Mo/ZSM-5    | 200         | 225         | 270         | 174          |

*TOF was measured at 240 °C.

The Pt content and acid content could be the key factors that influence the activity of propane combustion [15,21]. Kobayashi et al. [34] found a strong acid site was a factor that had great impact on the activity of supported Pt catalysts. In this work, the doping of Mo species only changed the content of weak acid sites and had a negligible effect on the content of strong acid sites. In Figure 7,
the Pt$^0$ content and weak acid content in the catalyst are plotted on the abscissa and the TOF value of the propane catalytic combustion at 240 °C was plotted on the ordinate to obtain the relationship between TOF-Pt$^0\%$ and TOF-weak acidity. It can be observed that the TOF value and the Pt$^0$ content were basically positively correlated with a nearly linear relationship, while there was no direct positive correlation between the weak acid content of the catalyst and the TOF value. The results showed that the improvement in the catalytic activity of the Pt-Mo/ZSM-5 catalyst should be related to the increase in the Pt$^0$ content, while the increased weak acid amount had little effect on the catalytic activities. After Mo doping, Mo and Pt interacted with each other and Pt species were easily be reduced. As a result, the content of Pt$^0$ in the catalyst increased and the catalyst activity was improved. The most active Pt-6Mo/ZSM-5 had the highest Pt$^0$ content.

Figure 7. Influence of the relative surface concentration of Pt$^0$ (a) and weak acidity (b) over the Pt-Mo/ZSM-5 catalysts on the TOF.

In order to further study the mechanism of Mo doping in Pt-6Mo/ZSM-5 in propane combustion, the Pt/ZSM-5 and Pt-6Mo/ZSM-5 catalysts were characterized by in-situ diffuse reflectance infrared transform spectroscopy (in situ DRIFTs). In Figure 8, the strong peaks at 2972, 2902 and 2870 cm$^{-1}$ were assigned to the vibration of C-H bond [35], which reflected the adsorption of gaseous propane on the catalyst. It can be clearly observed that at 150°C, the peak intensity of Pt-6Mo/ZMS-5 at this position was higher than that of Pt/ZSM-5, indicating that more propane was adsorbed on the surface of Pt-6Mo/ZSM-5. The peaks at 1576 and 1473 cm$^{-1}$ were assigned to the vibration of COO$^-$ in formed reaction intermediates [36]. The peaks of other possible oxidation products such as acrylic acid, acetone and other intermediates had not been observed. It might be due to the rapid dissociation and subsequent oxidation of the C-H bond of propane after activation [37], so only free formic acid species can be observed. The peaks of propane and reaction intermediates on both catalysts decreased with the increase in temperature. The peaks of propane on Pt-6Mo/ZSM-5 disappeared at 350 °C, while they were still visible on Pt/ZSM-5 at 350 °C. Likewise, almost no infrared peak of the intermediates on Pt-6Mo/ZSM-5 was observed at 350 °C, while some small picks on Pt/ZSM-5 still existed.
These results indicated that Pt-6Mo/ZSM-5 had better propane adsorption capacity and catalytic combustion activity than Pt/ZSM-5. Propane and the intermediates could be completely oxidized at relatively low temperatures over Pt-6Mo/ZSM-5. The formation of other intermediates was not observed, indicating that the addition of Mo to Pt/ZSM-5 catalyst did not change the reaction path of propane catalytic combustion.

2.4.2. Stability of Propane Catalytic Combustion

The results of stability tests for Pt/ZSM-5 and Pt-6Mo/ZSM-5 in propane combustion are shown in Figure 9. Both catalysts showed good stability at 300 °C. During the 80 h of continuous reaction, the activity of the catalysts did not decrease. The conversion of propane on Pt-6Mo/ZSM-5 was stable at about 99%, while that on Pt/ZSM-5 catalyst was stable at about 93% (Figure 9a). Figure 9b showed the catalytic activity of the catalysts under alternating temperatures. The activity of Pt-6Mo/ZSM-5 was stable at 240 °C and 550 °C, while the activity of Pt/ZSM-5 was stable at 550 °C and decreased slowly with the time on stream at 260 °C. The results indicate that Pt/ZSM-5 catalyst has good stability and its stability could be further enhanced by Mo doping.

In actual industrial applications, catalysts need to withstand higher temperatures, so the catalysts were subjected to a high-temperature aging treatment at 700 °C for 12 h. The catalytic combustion activities of propane before and after aging were shown in Figure 10. After aging, both catalysts had a certain degree of activity decline, but the decline of Pt-6Mo/ZSM-5 was less than that of Pt/ZSM-5. The T90 of Pt-6Mo/ZSM-5 increased by 25 °C after aging while that of Pt/ZSM-5 increased by 50 °C. This shows that the incorporation of Mo increases the high-temperature stability of Pt/ZSM-5.
The results of catalyst stability experiments showed that Mo doping not only improved the catalyst activity, but also improved the catalyst stability.

Figure 10. The propane catalytic combustion activity of Pt/ZSM-5 and Pt-6Mo/ZSM-5 before and after aging at 700 °C for 12 h.

3. Materials and Methods

3.1. Catalyst Preparation

The Pt-Mo/ZSM-5 catalyst was synthesized by the co-impregnation method. First, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (Sinopharm, Shanghai, China) was dispersed in deionized water and kept stirring until it was completely dissolved. Aqueous H$_2$PtCl$_6$ (Sinopharm, Shanghai, China) solution was added to the solution under stirring. Then, H-ZSM-5 (Nankai University Catalyst, Tianjin, China, SiO$_2$/Al$_2$O$_3$ = 80) was added to the mixed solution, keeping stirring for 2 h. The solution was evaporated by a rotary evaporator in a 60 °C water bath, and the sample was transferred to a crucible and dried at 110 °C for 12 h. Next, the sample was placed in a muffle furnace at 400 °C for 4 h. Pt-Mo/ZSM-5 series catalysts with platinum loadings of about 1 wt.% and different molybdenum loadings (2–8 wt.%) were obtained, and marked as Pt-nMo/ZSM-5 (n = 2, 4, 6, 8). The reference catalysts Pt/ZSM-5 and 6Mo/ZSM-5 were synthesized in a similar way.

3.2. Catalyst Characterization

The XRD patterns were tested by the D8 X-ray diffractometer (Bruker, Karlsruhe, Germany), using Cu Kα radiation (λ = 0.15406 nm, 40 kV, 40 mA) and 2θ was from 5° to 90°. X-ray fluorescence (XRF) was tested by the S4EXPLOPRER X-ray diffractometer (Bruker, Karlsruhe, Germany). The BET surface areas and volume of pores were measured by nitrogen adsorption/desorption on ASAP 2020 Plus automatic surface analyzer (Micromeritics, Norcross, GA, USA). HRTEM images were measured on a JEM-2001 microscope (JEOL, Tokyo, Japan). XPS characterization was performed on an Axis Ultra Dld spectroscopy (Kratos, Manchester, UK) with the Al Kα source of 1486.6 eV. Raman spectra were performed by the laser (λ = 532 nm) on a JEM2010 spectrometer (JEOL, Tokyo, Japan). H$_2$-TPR was performed on the ChemiSorb 2720 instrument (Micromeritics, Norcross, GA, USA). An amount of 50 mg catalyst was pretreated by helium for 1h at 180 °C and cooled down to room temperature. The catalyst was purged with 10%H$_2$/He (total rate = 30mL/min) and the temperature increased from 50 to 850 °C at the rate of 10 °C/min. CO-Chemisorption was measured on the ChemiSorb 2720 instrument (Micromeritics, Norcross, GA, USA). NH$_3$-TPD was performed on a Autochem II 2920 instrument (Micromeritics, Norcross, GA, USA). in situ DRIFTs were measured by a Nicolet 6700 instrument (ThermoFisher, Waltham, MA, USA). After background collection, the catalysts were
tested at the atmosphere of 1600 ppm C₃H₈, 2% O₂ and N₂ in balance by measuring 32 scans at 4 cm⁻¹ resolution.

3.3. Catalytic Activity Measurement

The activities for propane catalytic combustion were evaluated in the fixed bed reactor including stainless steel equipped with a quartz tube (i.d. 9 mm). Amounts of 200 mg catalysts (40–60 mesh) mixed with 800 mg quartz sand could be used in each test. The catalysts were pretreated at 400 °C in N₂ condition for 2 h and then cooled down to RT. The reactant component consisted of 1600 ppm C₃H₈, 2% O₂ and N₂ in balance and the total flow was 120 mL/min. The catalysts were stable and the same catalyst was employed for reaction under the range of temperatures. The results were analyzed online by Trace GC Ultra equipped with TCD and FID. No possible by-products, like propene and carbon monoxide were observed in the results. The conversion of propane at each temperature was stable for 30 min and was calculated as:

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\text{Conversion (propane)} = \frac{\text{propane}_{\text{in}} - \text{propane}_{\text{out}}}{\text{propane}_{\text{in}}} \times 100\%
\]

4. Conclusions

Pt-Mo/ZSM-5 catalysts with different Mo doping were synthesized by the co-impregnation method and applied to the reaction of propane catalytic combustion. The promotional effects of Mo doping on the Pt/ZSM-5 were investigated. Various characterization analyses demonstrated that there was an obvious interaction between Mo and Pt species. Mo doping made Pt species reduce easily and increased the content of Pt⁰ on the catalyst. There was a nearly linear relationship between the content of Pt⁰ and the TOF value of the catalyst, indicating that Pt⁰ was the active center of the catalyst. Among different proportions of Mo doping, Pt-6Mo/ZSM-5 exhibited the best activity. The T_{10}, T_{50} and T_{90} of Pt-6Mo/ZSM-5 dropped 50 °C, 40 °C and 40 °C respectively compared with those of Pt/ZSM-5. The TOF value of Pt-6Mo/ZSM-5 at 240 °C was almost three times that of Pt/ZSM-5. Mo doping not only improved the activity of the catalysts, but also improved the stability of the catalysts. The Pt-6Mo/ZSM-5 catalyst had excellent catalytic stability even after aging, thus has good potential in industrial applications.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/12/1377/s1, Figure S1: Particle size distribution of Pt particles on Pt-Mo/ZSM-5 catalysts with different Mo amounts, Figure S2. Al 2p and Pt 4f XPS spectra of (a) ZSM-5 and (b) Pt/ZSM-5. (c) Pt 4f spectra obtained by deducting a from b. Table S1. FWHM of Pt with different oxidation state in Pt-Mo/ZSM-5 catalysts.

Author Contributions: Z.L. performed the experiments and wrote the paper; K.Z. contributed analysis tools; W.S. (Wenjie Sun) contributed materials; H.X. conceived the project; Z.H. and W.S (Wei Shen), revised the paper. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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