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An excellent support of Pd catalyst for methane combustion: Thermal-stable Si-doped alumina

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Abstract

Thermal-stable Si-doped alumina was prepared by the reverse microemulsion method and was used as the support of Pd catalyst for the methane combustion. The physicochemical properties of Si-alumina and catalytic performance of Pd/Si-Al_2O_3 were characterized by XRD, N_2 adsorption, FT-IR, XPS and methane catalytic combustion. The results indicate that the presence of Si can increase the thermal stability of alumina and promote the coordination state of aluminum from tetrahedral to octahedral, but its content added should be controlled appropriately to 5–6 wt%. Si-doped alumina prepared by the reverse microemulsion method is an excellent support of Pd catalyst for the methane combustion, which can increase both the catalytic activity and thermal stability of the Pd catalyst. The studies also show that the calcination temperature of support affects remarkably the performance of catalyst, and the high thermal stability of support is very important to increase the performance of Pd catalyst for the methane combustion.

Keywords: Thermal stability; Si-doped alumina; Methane combustion; Pd catalyst; Reverse microemulsion method

1. Introduction

An interest in the catalytic combustion of methane arises from two reasons, one is to use it as the model reaction for abatement of volatile organic compounds (VOC), and another is to use the methane to power generation. The high catalytic activity and enough thermal stability are required for an excellent catalyst to catalyze combustion of methane. However, it is difficult for a catalyst to have these two requirements at the same time. In general, the supported noble metals catalysts, such as Pd and Pt, show a higher activity, but lower thermal stability, and the limited supply restricts the use of noble metals [1–6]. In order to improve the thermal stability of the noble metal catalysts, researchers have paid much attention to studying the efficient support [7–12]. Transition alumina has been used extensively as the support of noble metal catalyst due to its higher surface area, moderate chemical activity and lower cost [13–15]. But transition alumina will transfer inevitably to corundum after calcination at higher temperature, while its surface area and pore volume decreases significantly. Therefore, increasing the thermal stability of alumina is of primary industrial interest. Generally, the stabilization of alumina can be promoted by doping it with foreign elements such as alkaline-earth metals, rare-earth metals [16] and silicon [17–19], and by using a special synthesis method or by a combination of two means above [17–23]. Our studies [24] show that the reverse microemulsion method is a good method to synthesize the high thermal-stable alumina-substrate materials, and silicon is an effective doping element to improve the thermal stability of alumina. The advantages of the reverse microemulsion method lie in the fact that the formation of particles is confined within the reverse micelles, thus nano-structure materials with controllable particle size and shape and higher thermal stability can be obtained.

Herein, a series of Si-doped alumina (Si–Al–O) with high thermal stability was prepared by the reverse microemulsion method, and the effect of Si and its content on the structure characters and thermal stability have been studied. Using high thermal-stable Si-doped alumina as the support, the high

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efficient supported palladium catalysts for methane combustion have been developed.

2. Experimental

Si-doped alumina was prepared by the reverse microemulsion method, and the preparation procedure was the same as Ref. [24]. First, the reverse microemulsion (I) of aluminum nitrate, ethyl silicate (as additive), polyethylene glycol octylphenyl ether (as surfactant), cyclohexane (as oil phase), 1-hexanol (as co-surfactant) was prepared. Secondly, the reverse microemulsion (II) of ammonia, polyethylene glycol octylphenyl ether, cyclohexane, 1-hexanol was prepared. And then the reverse microemulsion (I) was mixed with (II) to react. After the precipitates formed were filtered, the solid was dried at 100 °C for 12 h and calcined in air at 800–1200 °C. This Si-doped alumina was marked as Si(*Z*)–Al–O, in which *Z* represents the Si content (wt%) and when $Z = 0$, Si(0)–Al–O is pure alumina prepared by the reverse microemulsion method. As the reference sample of conventional alumina, Al_2O_3(B) was prepared by calcining boehmite at high temperature directly.

Supported Pd catalysts were prepared by the wet impregnation method. $PdCl_2$ weighed was dissolved in nitric acid aqueous solution, and then Al_2O_3(B) or Si(5.2)–Al–O support (20–40 mesh) was added into the solution containing Pd above under ultrasonic concussion. After dried in vacuum, the catalyst was calcined in air at 550 °C (or 1100 °C) for 5 h. The Pd loading is 0.2 wt%.

The BET surface area of the sample was measured by the ST-03A Instrument of Surface Area and Pore Size Distribution (Beijing Analytic Instrument Plant) at liquid-N_2 temperature. X-ray diffraction (XRD) of the sample was analyzed by the Rigaku D/max/2550/PC, Cu Kα radiation. The X-ray photoelectron spectroscopy (XPS) spectrum of sample was performed on a VC Escalab II spectrometer using monochromatic Mg Kα radiation ($h\nu = 1253.6$ eV) at 1×10^{-10} Torr. Electrostatic surface charging was observed in all investigated samples owing to their poor electric conductivity. The binding energy (BE) of adventitious C 1s (284.8 eV) was used as a reference. The binding energy measured is accurate to ±0.2 eV. The surface composition of sample was calculated by the photoelectron peak area of each element in the XPS spectrum.

The catalytic activity of the catalyst for methane combustion was tested in the fixed bed reactor system with 0.1 g catalyst. The catalyst was made into pellet without any binder and crushed to 20–40 mesh. A feed mixture gas consisted of 4% (volume) methane, 86% nitrogen and 10% oxygen and GHSM was 42,000 ml g^{-1} h^{-1}.

3. Results and discussion

3.1. XRD patterns of Si-alumina

The XRD patterns of Si-doped alumina and alumina derived from boehmite are shown in Fig. 1. The diffraction peaks of

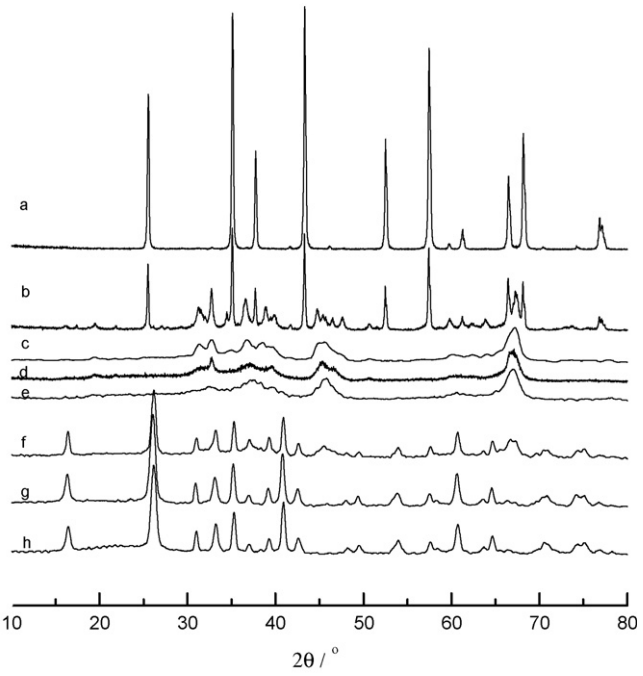

Fig. 1. XRD patterns of Al_2O_3(B) (a) and Si-alumina with the Si content of 0% (b), 2.5% (c), 5.2 (d), 6.1% (e), 10% (f), 15% (g) and 20% (h) after being calcined at 1100 °C for 10 h.

Al_2O_3 (a) derived from boehmite locates at $2\theta = 43.3°$, 35.1°, 57.5°, 25.6°, 68.2° and 52.5°, which are the same as the diffraction peaks of α-alumina. Al_2O_3 (b) prepared by a reverse microemulsion method exists in the α phase and θ phase ($2\theta = 67.2°$, 32.7°, 38.8°, 47.6° and 61.2°). This result proves that the phase transformation temperature of alumina prepared by the reverse microemulsion method is much higher than that of conventional alumina.

After Al_2O_3 is doped with Si, their XRD diffraction peaks have changed noticeably. When the content of Si is less than 6.1 wt%, there are very weak diffraction peaks of transition alumina including γ, δ and θ phases, and no trace of α phase; when the content of Si is more than 10 wt%, the mullite phase has been formed ($2\theta = 16.7°$, 26.5°, 31.2°, 33.5°, 35.5°, 39.5°, 41.2°, 42.8°, 48.5°, 50.4°, 54.5°, 57.8°). This shows that the presence of Si can enhance effectively the phase transformation temperature of alumina by forming the mullite phase. In the sample with lower Si content, even if this mullite phase is formed, it cannot be observed in the XRD patterns. This may be ascribed to its low content and high disperse. Jin et al. [25] and Hyatt et al. [26] also found that the presence of Si in alumina can enhance the crystallizing temperature of γ-, δ-, θ- and α-alumina by alloying of Si^{4+} into alumina.

3.2. BET surface area of Si-alumina

The BET surface areas of Si-alumina with different Si content and alumina derived from boehmite are shown in Table 1. The results show that, after being calcined at 1100 °C for 10 h, the surface area of alumina prepared by a reverse

Table 1
BET surface area of the Si-doped alumina and alumina derived from boehmite

Sample	Content of Si (wt%)	S_{BET} ($m^2\ g^{-1}$)		
		1100 °C/10 h	1150 °C/2 h	1200 °C/2 h
Al_2O_3(B)	0	14	–	–
Si(0)–Al–O	0	54	26	10
Si(2.5)–Al–O	2.5	123	111	103
Si(5.2)–Al–O	5.2	175	168	159
Si(6.1)–Al–O	6.1	156	153	137
Si(10)–Al–O	10	138	141	64
Si(15)–Al–O	15	90	73	50
Si(20)–Al–O	20	50	20	18

microemulsion method is much higher (54 $m^2\ g^{-1}$) than that of alumina derived from boehmite. This indicates that using appropriate preparation method to synthesize alumina may reduce the sintering and phase transformation of alumina at high temperature to keep its high surface area.

For the Si-alumina samples calcined at 1100–1200 °C, the effects of the Si content on their surface areas are shown in Table 1. With an increase of Si content, the surface area of Si-alumina increases greatly; when the Si content is 5.2 wt%, the surface area of Si(5.2)–Al–O reaches maximum, e.g. after calcination at 1100 °C for 10 h, its surface area is 175 $m^2\ g^{-1}$, and even after calcination at 1200 °C for 2 h, its surface area can be kept at 159 $m^2\ g^{-1}$. As the Si content is more than 5.2 wt%, the surface area of Si-alumina decreases with an increase of Si content. The higher the Si content, the lower its surface area is. When Si content is 20 wt%, the surface area of Si(20)–Al–O is less than that of Si(0)–Al–O, e.g. after being calcined at 1100 °C for 10 h, the surface area of Si(0)–Al–O is 54 $m^2\ g^{-1}$ and Si(20)–Al–O is only 50 $m^2\ g^{-1}$.

The results above show that, the presence of Si not only can enhance the crystallizing temperature of α-alumina, but also can restrict a growth of alumina grain by Si doping to alumina to protect the loss of the surface area at high temperature. When the content of Si added is much higher, the mullite crystalline phase would form and lead to the decrease of its surface area.

3.3. FT-IR spectra of Si-alumina

As shown in Fig. 2, there is an intense asymmetric absorption peak at 1110 cm^{-1} with a shoulder at ~1220 cm^{-1} and two absorption peaks at 804 cm^{-1} and 464 cm^{-1} in the FT-IR spectrum of pure SiO_2 calcined at 1100 °C for 10 h, which are related to strongly bonded Si–O–Si bridges in typical SiO_2 [27]. For the Si-doped alumina, the samples with a higher Si content (>10 wt%) have those absorption peaks and the intension of peaks is a function of the silicon content. This indicates that in the Si–Al–O sample with <10 wt% Si, the Si cations exist as the bridges of Si–O–Al bonded by the chemical combination between SiO_2 and Al_2O_3 and not as the bridges of Si–O–Si. For the Si–Al–O sample with >10 wt% Si, some SiO_2 exists as the bridges of Si–O–Si, except for some SiO_2 reacting with Al_2O_3 to form the bridges of Si–O–Al.

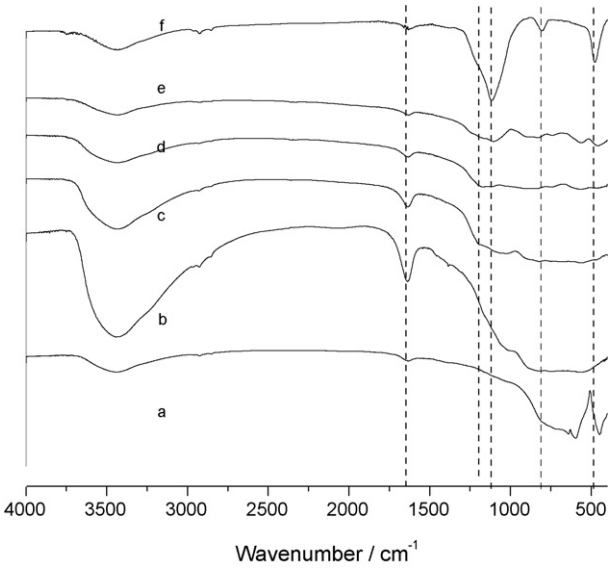

Fig. 2. FT-IR spectra of Si-doped alumina calcined at 1100 °C for 10 h with the Si content of 0% (a), 5.2 (b), 10% (c), 15% (d), 20% (e) and pure SiO_2 (f) calcined at 900 °C for 6 h.

The results above show that, the high thermal-stable Si-doped alumina can be prepared by the reverse microemulsion method. In order to investigate the performance of Si-doped alumina, it was used as the support of Pd catalyst for methane combustion.

3.4. Catalytic performance of supported Pd catalyst for methane combustion

Table 2 gives the catalytic performance of Pd catalysts supported on Si-alumina (Si(5.2)–Al–O) and alumina derived from boehmite (Al_2O_3(B)) for methane combustion. The results show that 0.2% Pd/Si(5.2)–Al–O has higher catalytic activity than 0.2% Pd/Al_2O_3(B) under the same reaction conditions, e.g. T_{50} (the reaction temperature at 50% conversion of methane) of 0.2% Pd/Si(5.2)–Al–O(800)–550, 0.2% Pd/Si(5.2)–Al–O(800)–1100 and 0.2% Pd/Si(5.2)–Al–O(1100)–550 is 492 °C, 530 °C and 410 °C, respectively, which is 28 °C, 51 °C and 59 °C lower than T_{50} of 0.2% Pd/Al_2O_3(B)(800)–550, 0.2% Pd/Al_2O_3(B)(800)–1100 and 0.2% Pd/Al_2O_3(B)(1100)–550, respectively. So Si(5.2)–Al–O is a more excellent support than Al_2O_3(B) for Pd catalyst used in methane combustion.

Table 2
BET surface area and catalytic activity of supported Pd catalysts for methane combustion

Catalyst	S_{BET} ($m^2\ g^{-1}$)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)
0.2% Pd/Si(5.2)–Al–O(800)[a]–550[b]	260	434	492	520
0.2% Pd/Al_2O_3(B)(800)–550	150	446	520	550
0.2% Pd/Si(5.2)–Al–O(800)–1100	115	428	530	583
0.2% Pd/Al_2O_3(B)(800)–1100	10	486	581	>700
0.2% Pd/Si(5.2)–Al–O(1100)–550	116	335	410	485
0.2% Pd/Al_2O_3(B)(1100)–550	15	370	469	550

[a] Support was calcinated at 800 °C for 4 h.
[b] Catalyst was calcinated at 550 °C for 5 h.

The results in Table 2 also show that, the effect of the calcination temperature of catalyst on its performance is remarkable. An increase of the calcinations temperature makes the sintering and volatilization of Pd active sites, leading to a decrease of the performance of catalyst. But the loss of catalytic activity of Pd supported on Si-doped alumina is lower than that on Al_2O_3(B). For example, T_{50} of 0.2% Pd/Al_2O_3(B)(800)–1100 is 61 °C higher than T_{50} of 0.2% Pd/Al_2O_3(B)(800)–550, and T_{50} of 0.2% Pd/Si(5.2)–Al–O(800)–1100 is 38 °C higher than T_{50} of 0.2% Pd/Si(5.2)–Al–O(800)–550.

As shown in Table 2, the calcination temperature of support affects the performance of catalyst noticeably. When the catalysts were calcined at the same conditions (such as 550 °C for 5 h), the higher the calcination temperature (such as 1100 °C/10 h) of support, the higher the catalytic activity of catalyst is, such as, T_{50} of 0.2% Pd/Al_2O_3(B)(1100)–550 is 51 °C lower than that of 0.2% Pd/Al_2O_3(B)(800)–550 and T_{50} of 0.2% Pd/Si(5.2)–Al–O(1100)–550 is 82 °C lower than that of 0.2% Pd/Si(5.2)–Al–O(800)–550. This is because that alumina calcined at high temperature is more stable, which leads to a less change of its structure and less interaction between Pd and support during the treatment process of catalyst, to keep a high dispersion of Pd on the support.

The results above show that the high thermal stability of support is very important for a high performance Pd catalyst used in the combustion of methane; the Pd catalyst supported on Si–Al–O has not only the high thermal stability but also a high catalytic activity for the combustion of methane.

3.5. BET surface area of supported Pd catalyst

The BET surface areas of the Pd catalysts are listed in Table 2. Under the same calcination conditions of the support and catalyst, the surface area of Pd catalyst supported on Si(5.2)–Al–O is much higher than that on Al_2O_3(B). This may be one reason that the catalytic activity of the former is higher than that of the latter for methane combustion. However, it is not concluded that the catalyst having high surface area is always accompanied with high catalytic activity for the methane combustion, because the reasons of affecting the activity of catalyst are more complicated. For example, the surface area of 0.2% Pd/Si(5.2)–Al–O(800)–550 and 0.2% Pd/Al_2O_3(B)(800)–550 is much higher than that of 0.2% Pd/Si(5.2)–Al–O(1100)–550 and 0.2% Pd/Al_2O_3(B)(1100)–550, respectively, but the catalytic activity of the latter is higher or comparable to the former. The presence of this phenomenon above is because that alumina treated at low temperature is not as stable as that treated at high temperature; when it is used as the support of catalyst, its structure would be changed during thermal atmosphere; this change of structure may lead to the strong interaction between alumina and palladium, which makes its catalytic activity reduce.

3.6. XRD patterns of supported Pd catalysts

Fig. 3 shows the XRD patterns of different catalysts. Besides the diffraction peaks of alumina crystalline phase, there is no trace of palladium or palladium oxide phase, which ascribes to the lower loading and high dispersion of Pd. Compared with the XRD patterns of the alumina support, the alumina crystalline phase in the catalysts (calcined at 550 °C for 5 h) has no obvious change (the figure has been omitted here). Although the crystalline forms of alumina in 0.2% Pd/Si(5.2)–Al–O(800)–550, 0.2% Pd/Si(5.2)–Al–O(1100)–550 and 0.2% Pd/Al_2O_3(B)(800)–550 are all transition (γ, δ, θ)-alumina, their catalytic activities are much different. For 0.2% Pd/Al_2O_3(B)(1100)–550 and 0.2% Pd/Al_2O_3(B)(800)–550, the alumina crystalline phases of two supports are different, the former displays as α phase and the latter displays as transition phase (γ, δ and θ), but the catalytic activity of the former is higher than the latter. For 0.2% Pd/Si(5.2)–Al–O(1100)–550 and 0.2% Pd/Al_2O_3(B)(1100)–550, the former displays as transition phase (γ, δ and θ) and the latter displays as α phase, but the catalytic activity of the former is higher than the latter.

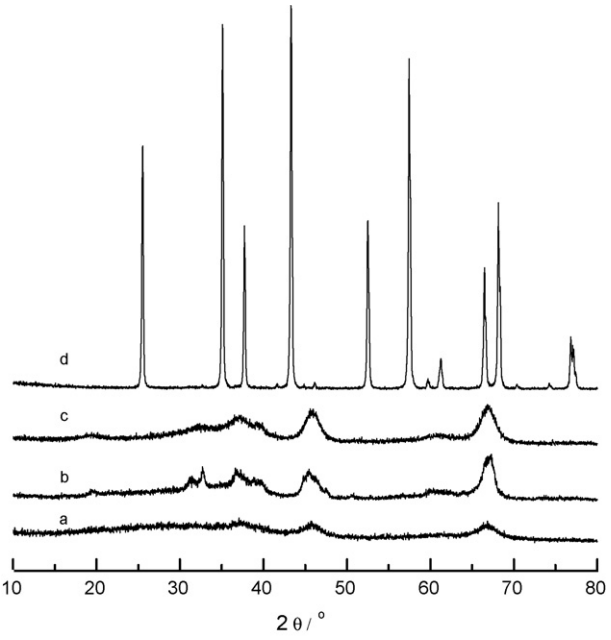

Fig. 3. XRD patterns of 0.2% Pd supported on Si(5.2)–Al–O(800*) (a), Si(5.2)–Al–O(1100) (b), Al_2O_3(B)(800) (c), and Al_2O_3(B)(1100) (d) (*the calcination temperature of support; catalysts were calcined at 550 °C for 5 h).

These results indicate that the alumina crystalline phase of support is not the main impact factor of catalytic activity of Pd/Al_2O_3 for the methane combustion, that is, there is no direct relationship between alumina crystalline phase and catalytic activity.

3.7. XPS study of supported Pd catalysts

The XPS spectra of supported Pd catalysts are shown in Figs. 4–6. As the Pd loading is very low, the peaks of Pd are hardly observed in the XPS spectra.

The O 1s spectra in Fig. 4 show that, the O 1s binding energy (BE) of Al_2O_3(B) is 530.5–530.6 eV and that of Si(5.2)–Al–O is 531.2–531.7 eV. The difference between O 1s BEs is ascribed to the fact that O 1s binding energy of Si–O band is higher than that of Al–O band [28,29]. For the Pd/Si(5.2)–Al–O catalyst,

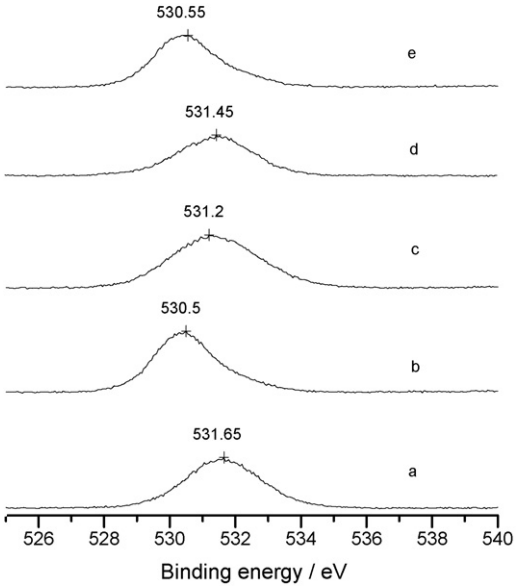

Fig. 4. O 1s XPS spectra of 0.2% Pd supported on Si(5.2)–Al–O(1100*)–550** (a), Al_2O_3(B)(1100)–550 (b), Si(5.2)–Al–O(800)–550 (c), Si(5.2)–Al–O(800)–1100 (1100) (d) and Al_2O_3(B)(800)–1100 (e) (*the calcination temperature of support; **the calcination temperature of catalyst, similarly herein after).

Fig. 6. Si 2p XPS spectra of 0.2% Pd supported on Si(5.2)–Al–O(1100)–550 (a), Si(5.2)–Al–O(800)–550 (b) and Si(5.2)–Al–O(800)–1100 (c).

there is a little difference of O 1s BE between three samples, which is caused by different calcination temperature.

Alumina in 0.2% Pd/Si(5.2)–Al–O(1100)–550 and 0.2% Pd/Si(5.2)–Al–O(800)–1100 has ever been treated at 1100 °C, and alumina in 0.2% Pd/Si(5.2)–Al–O(800)–550 has never been treated at 1100 °C. In the thermal treatment at high temperature, water is normally evolved from two neighboring hydroxyl ions that leave the coordination sphere of aluminum ion incompletely [30]. So that, the surface hydroxyl groups on alumina support disappear and the O 1s binding energy increases slightly.

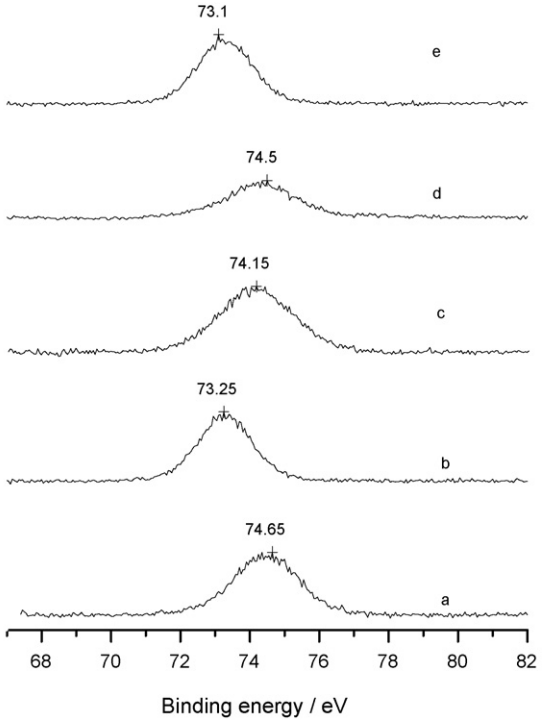

Fig. 5. Al 2p XPS spectra of 0.2% Pd supported on Si(5.2)–Al–O(1100)–550 (a), Al_2O_3(B)(1100)–550 (b), Si(5.2)–Al–O(800)–550 (c), Si(5.2)–Al–O(800)–1100 (d) and Al_2O_3(B)(800)–1100 (e).

The Al 2p XPS spectra of Al_2O_3(B) and Si-alumina are shown in Fig. 5. The Al 2p BE of Al_2O_3(B) is 73.1–73.3 eV and the Al 2p BE of Si-alumina is 74.2–74.7eV, which are corresponding to the tetrahedral and octahedral coordination aluminium, respectively [31]. This proves that the addition of silicon in alumina has changed the coordination state of aluminum, and leads to the change of Al 2p BE. Black et al. [32] also proved that adding silicon into alumina can vary the BE of Al 2p, the higher the ratio of Si/Al, the higher the BE is. Otherwise, enhancing the calcination temperature of alumina supports would increase Al 2p BE. For a little difference of Al 2p BE between three Pd/Si(5.2)–Al–O catalysts, it can be ascribed to the calcination at high temperature.

The results in Fig. 6 show that, the binding energy of Si 2p (101.8–102.6 eV) in three Pd/Si–Al–O catalysts is lower than that in SiO_2 (103.4 eV), which is an evidence for an incorporation of Si into alumina [32]. The Si 2p XPS spectrum of sample calcined at 800 °C has two peaks, and the samples calcined at 1100 °C has only one peak. This indicates that after the catalyst is calcined at high temperature, all silicon ions become almost one chemical state, that is, the coordination state of silicon is more homogeneous.

The studies of XPS above show that, adding silicon into alumina makes the coordination state of aluminum change from tetrahedral to octahedral, and the calcination at high temperature makes the coordination state of Si more homogeneous.

4. Conclusion

In summary, using the reverse microemulsion method we can prepare the high thermal-stable alumina substrate materials. The presence of Si can strongly improve the thermal stability of alumina, but the Si content affects greatly the structure properties and thermal stability of alumina and the most appropriate content of Si added is 5–6 wt%. The incorporation of silicon into alumina can vary the coordination state of aluminum from tetrahedral to octahedral, and the high temperature calcination helps to promote this change, while the coordination state of Si trends towards more homogeneous. Si-doped alumina prepared by the reverse microemulsion method is an excellent support of the Pd catalyst for the methane combustion. Addition of Si in alumina support can increase obviously the catalytic activity and thermal stability of Pd catalyst for the methane combustion.

Acknowledgements

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