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Thermal characterization of titania-modified alumina-supported palladium and catalytic properties for methane combustion

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Abstract

Thermal characterization of Pd/TiO_2-Al_2O_3 catalysts under oxygen or hydrogen atmosphere was investigated by means of thermogravimetry (TG), differential scanning calorimetry (DSC), temperature programmed reduction (TPR) and temperature programmed desorption (TPD). Further, the effects of titania on the catalytic property of Pd/Al_2O_3 towards methane combustion were also examined. A TG–DSC studies revealed that the heat evolved during oxygen adsorption at 25 °C depended on the crystallite diameter. TPR and TPD studies of oxidized samples also demonstrated that the coating of Pd/Al_2O_3 catalysts with titania can weaken the strength of the Pd–O bonds. Apparently the effect of coating Pd/Al_2O_3 catalyst with TiO_2 is the improvement of the methane combustion at lower temperatures. This is probably due to the decrease of the strength of the Pd–O bonds.

Keywords: Palladium; Methane combustion; Calorimetry; TPR; TPD

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1. Introduction

Supported palladium is a very active catalyst for the total oxidation of hydrocarbons. This is due to the fact that palladium shows a high capacity for being oxidized even under very fuel lean conditions unlike most other noble metal catalysts [1,2]. This high capacity has been attributed to the fact that not only metallic palladium but also palladium oxide are active oxidation catalysts. Although, this is still poorly understood.

Alumina, mainly γ-Al_2O_3, is widely used as support in the field of heterogeneous catalysis [3]. This is because alumina has strong Lewis acid centers [4] which addition to their intrinsic catalytic activity in several reactions, they are able to stabilize and disperse adequately a number of active phases, as well as to retain a high surface area at high temperatures strongly interacting with metal ions. However, in many cases, the catalytic activities of alumina-supported catalysts are lower than those of catalysts supported on other oxides, i.e. titania or zirconia [5,6]. To improve the catalytic activity and to modulate the surface acidity of the catalyst, alumina can be modified by other oxides. In a previous paper [7], we have shown that the coating of Pd/Al_2O_3 catalysts with titania can decrease the bond strength of Pd–O and promotes the reduction/decomposition of PdO into metallic palladium.

More recently, several studies have been reported an unusual activity of catalysts containing Pd for methane combustion [8–12]. Schwartz et al. [13] and Cullis and

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Willatt [14] reported the decrease of the methane combustion activity by the oxidation of palladium catalyst, suggesting that metallic palladium is the active phase. Contrary, Farrauto et al. [8] and McCarty [9] found PdO to be more active for methane combustion than metallic palladium. This opened up again the question whether PdO or metallic Pd is the active phase for hydrocarbon oxidation.

Therefore, we are interested in studying the thermal characterization and catalytic properties of Pd/Al_2O_3 coated with TiO_2 and find out if this fact can weaken the strength of the PdO bonds and, to promote the activity of modified Pd/Al_2O_3.

2. Experimental

2.1. Sample preparation

Titania-modified alumina supports ($x\%TiO_2$-Al_2O_3, with $x\%$ of TiO_2 in weight) of several TiO_2 loading were prepared by the impregnation of γ-Al_2O_3 (Kiaser, 234 $m^2\,g^{-1}$) with appropriate solutions of $Ti(i\text{-}OC_3H_7)_4$ in isopropanol. The impregnated samples were immediately after relieved of solvent overnight at 110 °C, calcined at 600 °C during 6 h and stored as carriers for preparing supported palladium catalysts. Palladium was introduced into various supports (Al_2O_3 and $x\%TiO_2$-Al_2O_3) by the wetness of the latter with hot H_2PdCl_4 solution. It was obtained slurries that were heated overnight at 110 °C and then calcined in air at 500 °C during 4 h before being stored as testing sample. These palladium catalysts are designated as fresh samples.

2.2. Thermal characterization

The isothermal energy changes and the amounts of oxygen uptake during the oxygen consumption were measured using a Setaram TG–DSC 111 dual port calorimeter. Before the consumption measurement, each $Pd/x\%TiO_2$-Al_2O_3 sample was pre-reduced in a hydrogen gas current at 150 °C (300 °C for Pd/Al_2O_3 samples) during 1 h following by the subsequent evacuation during 1 h at 200 °C (350 °C for Pd/Al_2O_3 samples). Fig. 1 presents a TG–DSC time profile on oxidizing 4.72%Pd/Al_2O_3 with oxygen at 25 °C.

Both TPR and TPD studies were performed on fresh catalysts in the same equipment. A 30 ml min^{-1} flow of 10% H_2–Ar was used to reduce the oxidized

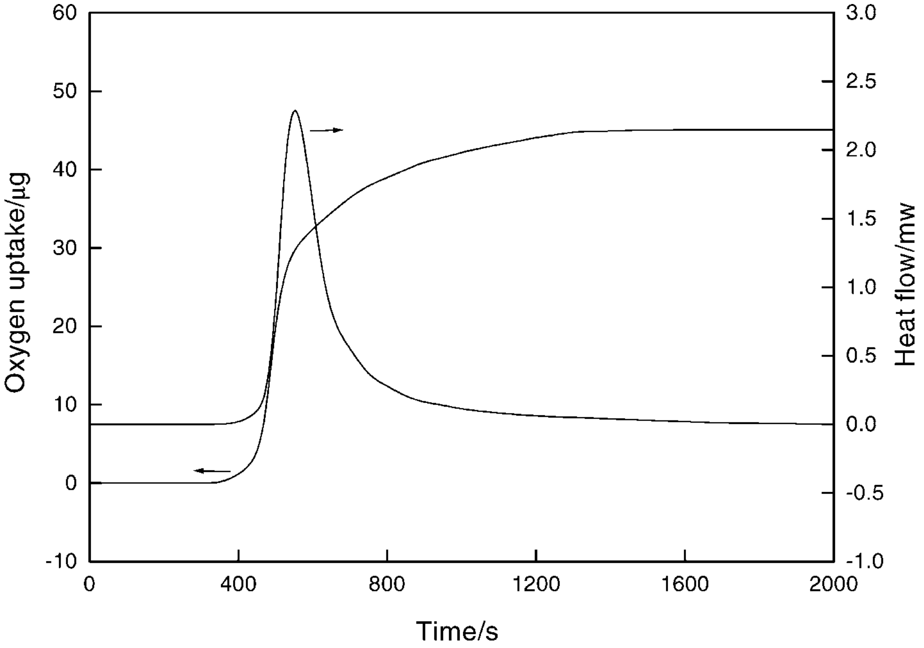

Fig. 1. The TG–DSC results of oxygen adsorption on 4.72%Pd/Al_2O_3 sample at 25 °C.

samples in TPR experiments. The rate of H_2 consumption was monitored by a thermal conductivity detector (TCD) as the temperatures of the samples were raised from −60 to 200 °C at a constant rate of 7 °C min^{-1}. A flow of He (purity 99.999%) was used in the TPD experiments to purge away the oxygen desorbed from the oxidized samples using a heating rate of 10 °C min^{-1} in the 25−900 °C temperature range. The rate of oxygen desorption was monitored by the TCD in the outlet He flow.

2.3. *Catalytic activities measurements*

The catalytic activities towards methane combustion were carried out in a fixed-bed reactor. The flow rate of the inlet gas (comprising 1/120 (v/v) of CH_4/air) was regulated at 120 ml min^{-1} with mass flow controller. The composition of the outlet gas was monitored continuously by a flame ionization detector (FID) in the 300–700 °C reactor temperature range at a rate of 5 °C min^{-1}. Conversion was defined by the fraction of methane consumption.

3. Results and discussion

3.1. *Thermal characterization*

The quantity of oxygen gas consumed in each adsorption, N_O^{ad}, is confined on the palladium metal surface and it is determined from the TG curves of the samples, according to the mass gain (Δm_{ox}) obtained after 2×10^3 s of oxygen chemisorption at 25 °C. The integral heats of adsorption (ΔH_{ad}) of oxygen and the average diameter (*d*, which was volumetrically determined by chemisorption of hydrogen at 25 °C under an assumption that $H/Pd^s = 1.1$ for the monolayer chemisorption) of palladium crystallites are shown in Table 1. According to the results, Fig. 2 correlates the $-\Delta H_{ad}$ with the average diameter of palladium crystallites dispersed on Al_2O_3 and TiO_2–Al_2O_3 supports. Apparently, the heat evolved during adsorption of oxygen on palladium crystallites varies significantly with the diameter of the crystallites and the kind of support. For Pd/Al_2O_3 catalysts, the evolved heats of adsorption increased about 100 kJ (mol O_2)$^{-1}$ as the size of palladium crystallites decreased from 8.0 to 1.5 nm. The crystallite size clearly affects the heats of oxygen adsorption on Pd/Al_2O_3 catalysts that may be due primarily to an electronic effect. However, for Pd/TiO_2-Al_2O_3, the evolved heats of adsorption increased only about 20 kJ (mol O_2)$^{-1}$ as the size of palladium crystallites decreased from 5.5 to 1.5 nm. In the small variations of ΔH_{ad} for oxygen adsorption on Pd/TiO_2-Al_2O_3 catalysts, crystallite size independence is assumed. Using a microcalorimetric study of the oxygen adsorption on alumina-supported palladium, Chou and Vannice [15] observed variations in the Pd–O bond strengths on supported palladium catalysts. They concluded that changes in the electronic properties of small palladium crystallites are mainly responsible for the observed increase in the Pd–O bond

Table 1
The average diameter of palladium crystallites and integral heats of adsorption of oxygen on palladium catalysts

Sample	Hydrogen chemisorption		Oxygen chemisorption	
	D	*d* (nm)	N_O^{ad}/N_{Pd}	$-\Delta H_{ad}$ (kJ (mol O_2)$^{-1}$)
0.96%Pd/20%TiO_2-Al_2O_3	0.80	1.4	0.46	285
1.02%Pd/10%TiO_2-Al_2O_3	0.75	1.5	0.49	282
0.98%Pd/6%TiO_2-Al_2O_3	0.60	1.8	0.41	280
1.10%Pd/TiO_2	0.50	2.2	0.31	272
1.95%Pd/TiO_2	0.33	3.3	0.22	265
2.47%Pd/TiO_2	0.20	5.5	0.13	270
1.08%Pd/Al_2O_3	0.80	1.4	0.48	346
1.07%Pd/Al_2O_3	0.52	2.1	0.33	334
0.98%Pd/Al_2O_3	0.38	2.9	0.27	308
4.72%Pd/Al_2O_3	0.21	5.2	0.14	293
10.09%Pd/Al_2O_3	0.14	7.9	0.10	253

D: dispersion of palladium metals; *d*: average particle size; N_O^{ad}/N_{Pd}: uptake of oxygen atoms on palladium at 25 °C.

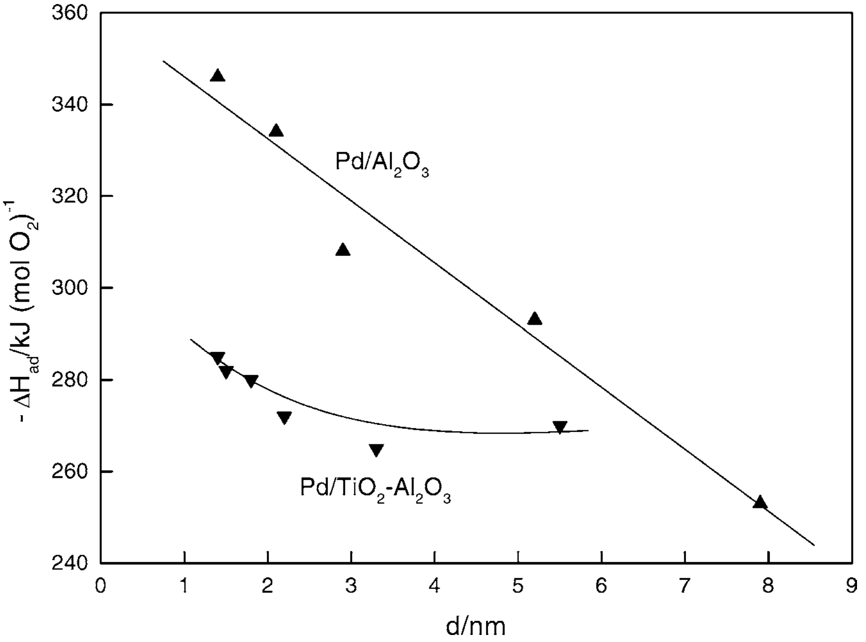

Fig. 2. Variations of $-\Delta H_{ad}$ of oxygen adsorption at 25 °C with the average diameter of various supported palladium metal crystallites: Pd/Al_2O_3 (▲); Pd/x%TiO_2-Al_2O_3 (▼).

strength. Comparison of the above values with the values here obtained for $-\Delta H_{ad}$ for oxygen adsorption on Pd/TiO_2-Al_2O_3, these latter values are smaller than that observed for Pd/Al_2O_3 probably due to significant differences in the strength of the Pd–O bonds. The coating of Pd/Al_2O_3 catalysts with TiO_2 can weaken the strength of the Pd–O bonds.

TPR is a technique of thermal analysis that monitors the rate of consumption of hydrogen by a sample in a range of increasing temperature. Fig. 3 displays a series of TPR spectrum of Pd/Al_2O_3, Pd/TiO_2 and Pd/x%TiO_2-Al_2O_3 fresh catalysts. Two peaks are noticed in TPR trace of 0.98%Pd/Al_2O_3, a peak near 40 °C due to the hydrogen consumption and a peak near 80 °C due to the hydrogen desorption. The first peak may have resulted from a consumption of hydrogen on the reduction of oxidized palladium.

$$H_2 + PdO \rightarrow Pd + H_2O \qquad (1)$$

The palladium crystallites, thus reduced, may absorb hydrogen to form “PdH” phase in hydrogen environment (depends on the pressure of hydrogen and the system temperature) [16]. According to the phase diagram of the Pd–H_2 system, palladium crystallites tend to absorb hydrogen to form Pd^bH_x or “PdH” at low temperature under $P_{H_2} = 1.0 \times 10^4$ Pa (the partial pressure of hydrogen in H_2–N_2 flow of TPR system), i.e.

$$xH_2 + 2Pd^b \Leftrightarrow 2Pd^bH_x \qquad (2)$$

The superscript b denotes palladium atoms in the bulk of palladium crystallites reduced according reaction 1, and the values adopted by subscript x depend on the temperatures. On raising the temperature above 80 °C, “PdH” in the flow of H_2–N_2 tends to desorb the hydrogen absorbed. The profile for 0.96%Pd/20%Ti-Al_2O_3 displays that an additional peak of hydrogen consumption occurs near 0 °C and the relative intensity of the peak near 40 °C decrease as the Pd/Al_2O_3 sample is modified with TiO_2. The temperature of this new peak is shifted to lower temperatures and its relative intensity is increased respect to that of the peak near 25 °C, as the content of TiO_2 in the catalyst is increased. The TPR profile for 1.10%Pd/TiO_2 shows that the catalyst is reduced below 0 °C. Apparently, observed changes of the TPR profiles in Fig. 3 indicate variations in the distribution of palladium oxide with support composition. The peak around 0 °C should be the PdO

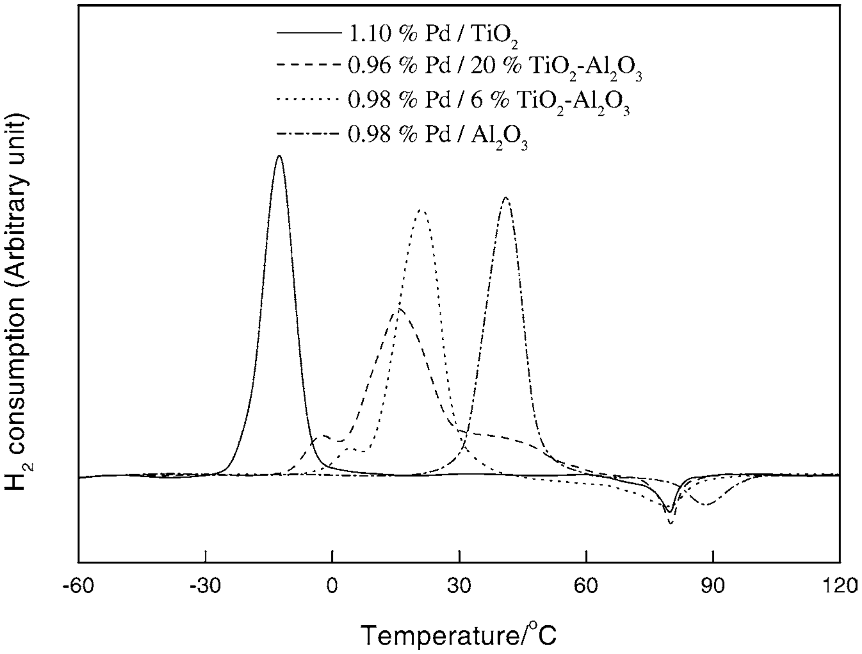

Fig. 3. TPR profiles for Pd/x%TiO_2-Al_2O_3 catalysts.

dispersed on titania-rich grains and the peak around 30 °C should be the PdO dispersed on alumina-rich grains. Probably, the coating of Pd/Al_2O_3 catalysts with TiO_2 can weaken the strength of the Pd–O bonds and decrease the reduction temperature.

The chemical behavior of supported palladium oxide is reported to be strongly dependent on the interaction between the palladium phase and the support [17–21]. The changes in the reactivity of PdO of the investigated catalysts can be exemplified by the course of the decomposition of palladium oxide. Apparently, the effect of TiO_2 coating on the strength of the Pd–O bonds can also be characterized with TPD technique. Fig. 4 shows a series of TPD spectra of oxygen obtained from Pd/x%TiO_2-Al_2O_3 fresh catalysts of various TiO_2 loads. The supported Pd/Al_2O_3 oxidized catalyst became unstable at $T > 800$ °C and was thermally decomposed into metallic palladium in the heating process according to reaction (3).

$$2PdO \rightarrow 2Pd + O_2 \quad (3)$$

The degree of the shift of the beginning decomposition temperature towards a lower value obviously increased from 800 to 550 °C with the TiO_2 loading x, with x from 0 to 100 in the Pd/x%TiO_2-Al_2O_3 catalysts. Because of the electronic property of supported palladium metal modified by TiO_2, the bond strength between Ti and Pd increases as the strength of the Pd–O bonds decrease. Similar conclusions can be extracted from the TPR data. It can be deduced that the coating of TiO_2 on Pd/Al_2O_3 catalysts can weaken the strength of the Pd–O bonds and enhances leading to its breaking at lower temperatures.

3.2. *Catalytic activities*

Catalytic combustion of methane has drawn great attention in recent years because methane is a well-known greenhouse gas and the most stable and abundant alkane. Therefore, it is interesting to study the catalytic properties on coating Pd/Al_2O_3 with TiO_2 and to determine if the weaken of the strength of the Pd–O bonds can promote the activity of Pd/Al_2O_3 towards methane combustion. The steady-state catalytic activities for methane combustion on Pd/x%TiO_2-Al_2O_3 samples are compared and given at increasing temperatures in Fig. 5. The temperatures required for 10% ($T_{10\%}$) and 50% ($T_{50\%}$)

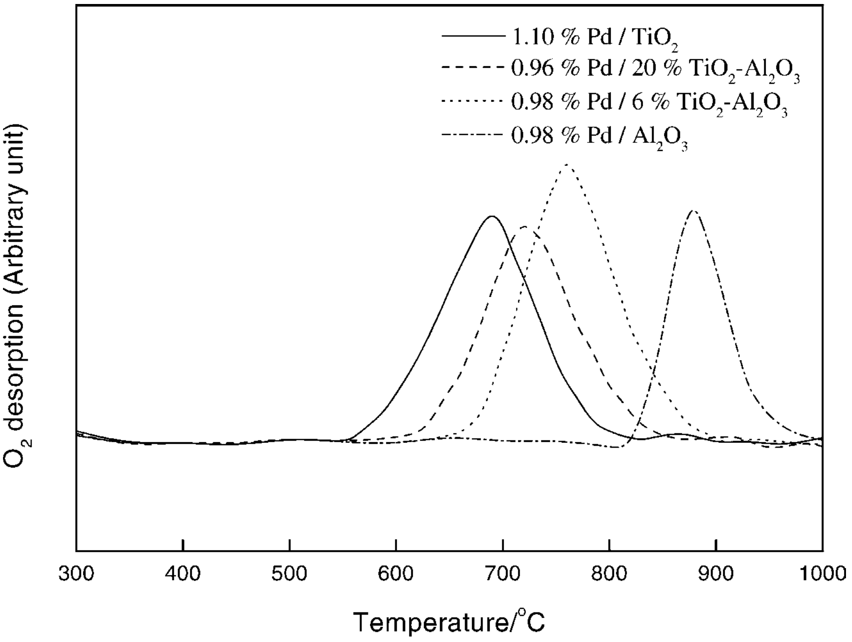

Fig. 4. Oxygen TPD profiles for Pd/x%TiO_2-Al_2O_3 catalysts.

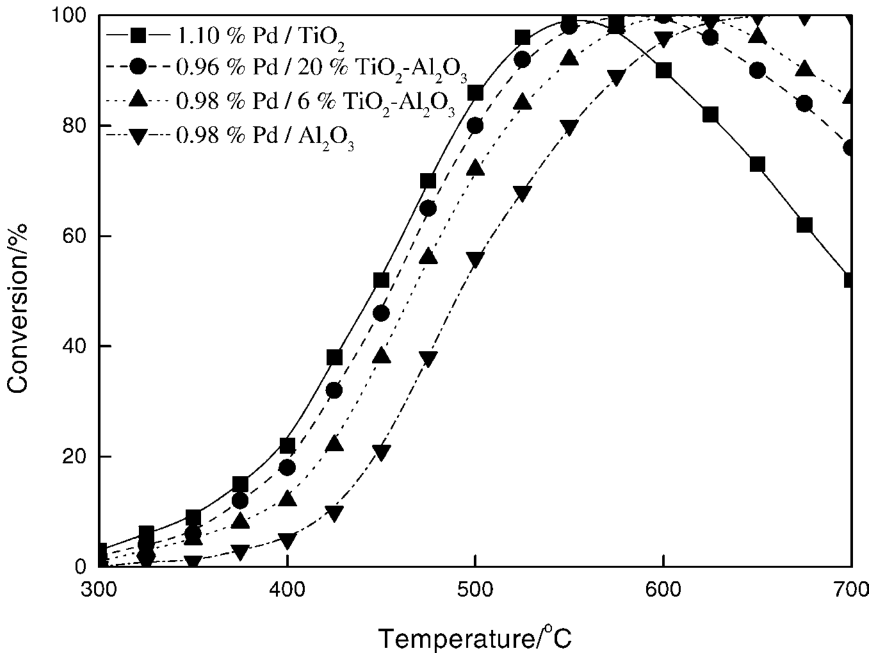

Fig. 5. The catalytic activities of Pd/x%TiO_2-Al_2O_3 catalysts on methane combustion.

Table 2
Hydrogen uptake on both fresh and aged Pd/x%TiO_2-Al_2O_3 catalysts at 25 °C

Sample	Treatment	Pd^sH	Pd^bH
4.85%Pd/TiO_2	Fresh	0.15	0.50
	After 750 °C reaction	0.10	0.50
	Recalcined at 500 °C	0.10	0.49
0.98%Pd/6%Ti-Al_2O_3	Fresh	0.60	0.32
	After 750 °C reaction	0.28	0.32
	Recalcined at 500 °C	0.28	0.30

Pd^sH: hydrogen adsorbed on palladium surface from H_2 chemisorption at $P_{H_2} = 10$ Torr and $T = 25$ °C. Pd^bH: hydrogen absorbed into the bulk of palladium crystallites from $P_{H_2} > 10$ Torr and $T = 25$ °C.

partial combustion of methane are 350 and 440 °C, respectively, for the 1.10%Pd/TiO_2 catalyst. While, the temperatures raise to 430 and 490 °C, respectively, for the 0.98%Pd/Al_2O_3 catalyst. This shows that a partially modified alumina by titania is beneficial in the methane combustion. According to the above thermal characterization, i.e. measurement of heat of adsorption of oxygen, TPR and TPD results, the temperatures for 10 and 50% partial combustion of methane are gradually lowered by increasing the loading amount of titania mainly due to a weakening in the strength of the Pd–O bonds by the presence of TiO_2.

The enhancement of the combustion activity with titania loading is apparent at lower temperature. But, the activity of titania coated catalysts cannot resist to higher temperatures and decay easily in case of a reaction temperature higher than 650 °C. The observed decay in activity of Pd/x%TiO_2-Al_2O_3 catalysts at higher temperatures may possibly result from moieties of TiO_2 inlaying the palladium crystallites. Table 2 lists the isotherm of hydrogen chemisorption on both fresh and aged Pd/x%TiO_2-Al_2O_3 catalysts. The absorbing hydrogen into the bulk of palladium crystallites (Pd^bH) remains unchanged since the hydrogen atom can dissolve gradually into the bulk. But, the adsorbing hydrogen on the palladium surface (Pd^sH, where the Pd^s is the palladium atoms on the surface) decreases for the aged catalysts. The decrease in Pd^sH can be regarded as a migration of TiO_2 during the agglomeration of TiO_2 on the palladium surface.

A strong interaction between metal (Pd) and support (TiO_2) that have been exposed to high temperatures has been proposed [22–25]. Jacobs and Schryvers suggested that the adsorbed hydrogen could be recovered and the aged catalyst transform into a fresh one when the aged sample are recalcined at 500 °C [25]. In the same condition, however, the aged samples in this study cannot be recovered after recalcined at 500 °C. Apparently, the strong metal support interaction has been excluded.

4. Conclusions

Thermal characterizations of supported palladium catalysts by TG–DSC, TPR and TPD data give some evidences for the character of the coating titania on the Pd/Al_2O_3 catalysts. These data reveal that the effect of coating titania on the Pd/Al_2O_3 catalysts results in the improvement of their catalytic activity for methane combustion at lower temperatures as the titania content increase. The enhancement effect is owing to the decrease in the strength of the Pd–O bonds that promotes the catalytic activity toward methane combustion at lower temperatures.

Acknowledgements

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