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$Al_{18}B_4O_{33}$ aluminium borate: A new efficient support for palladium in the high temperature catalytic combustion of methane

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Abstract

Well crystallised aluminium borate $Al_{18}B_4O_{33}$ has been synthesised from alumina and boric acid with a BET area of 18 m^2/g after calcination at 1100 °C. Afterwards, 2 wt.% $Pd/Al_{18}B_4O_{33}$ was prepared by conventional impregnation of $Pd(NO_3)_2$ aqueous solution and calcination in air at 500 °C. The catalytic activity of $Pd/Al_{18}B_4O_{33}$ in the complete oxidation of methane was measured between 300 and 900 °C and compared with that of Pd/Al_2O_3. $Pd/Al_{18}B_4O_{33}$ exhibited a much lower activity than Pd/Al_2O_3 when treated in hydrogen at 500 °C or aged in O_2/H_2O (90:10) at 800 °C prior to catalytic testing. Surprisingly, a catalytic reaction run up to 900 °C in the reaction mixture induced a steep increase of the catalytic activity of $Pd/Al_{18}B_4O_{33}$ which became as active as Pd/Al_2O_3. Moreover, the decrease of the catalytic activity observed around 750 °C for Pd/Al_2O_3 and attributed to PdO decomposition into metallic Pd was significantly shifted to higher temperatures (820 °C) in the case of $Pd/Al_{18}B_4O_{33}$. The existence of two distinct types of PdO species formed on $Al_{18}B_4O_{33}$ and being, respectively, responsible for the improvement of the activity at low and high temperature was proposed on the basis of diffuse reflectance spectroscopy and temperature-programmed desorption of O_2.

Keywords: Catalytic combustion; Methane; Palladium; Aluminium borate

1. Introduction

It is well known that methane is the hydrocarbon, the most resistant to oxidation [1]. When catalytically processed, combustion offers some advantages, such as complete oxidation without emission of unburnt hydrocarbon and carbon monoxide. Moreover, lower temperatures encountered due to lower fuel feed avoids any NO_x to be formed both thermodynamically and kinetically [2]. Transition metal ions containing catalysts have been used in methane combustion either as simple oxides [3] or as mixed oxides, such as spinels [4], perovskites [5] and hexaaluminates [6]. However, high temperatures induce a loss of activity due to the loss of BET area, the changes of structure, the segregation into several phases which are generally less active [7]. For Pd supported catalysts, alumina is generally used as support, but its structural transformation into α-alumina at high temperature leads to drastic BET area loss [8]. Many studies have been then devoted to alumina stabilisation by use of alkaline earth [9], rare-earth [10], silicon [11] or even zirconia [12].

On the other hand, it is known that some ceramics do have required properties for use as catalysts or supports in high temperature catalysis [13], but they have not been considered for use in catalysis: their propensity to sintering may have limited their use. For example, boron oxide and alumina lead to several stable phases having the general formulas $(Al_2O_3)_x(B_2O_3)_y$ [14]. The most thermally stable phase is $Al_{18}B_4O_{33}$ or $9Al_2O_3\ 2B_2O_3$ currently abbreviated as 9A2B. This phase was previously obtained with a fairly high specific surface [15]. It is a refractory ceramic which melts at 1450 °C without decomposition [16]. This light-weighted material ($\rho = 2.9$ kg/dm^3) has a rather low thermal expansion coefficient ($\sigma = 4.2.10^{-6}\ K^{-1}$) [16]. The 9A2B structure consists of tetrahedral AlO_4 and octahedral AlO_6 linked by planar BO_3 species. However, some AlO_5 species are also present as revealed by ^{27}Al MAS NMR [15].

The aim of the present work was to prepare $Al_{18}B_4O_{33}$ and to use this solid for supporting palladium. The catalytic activity of $Pd/Al_{18}B_4O_{33}$ in the methane catalytic combustion was measured up to 900 °C and compared to that of Pd/Al_2O_3.

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According to our knowledge, it is the first time that this support is used in catalytic combustion.

2. Experimental

2.1. Preparation

$Al_{18}B_4O_{33}$ was obtained by impregnating alumina with acid boric. A calculated mass of alumina was contacted at 60 °C for 1 h with a solution of boric acid containing the required amount of boron according to the final stoichiometry. The water was then removed at 60 °C under reduced pressure. The obtained solid was dried overnight at 120 °C, crushed and finally calcined in a vertically mounted quartz cell at 1100 °C during 12 h under flowing oxygen.

$Pd/Al_{18}B_4O_{33}$ (1.8 wt.% Pd) was prepared by support impregnation with $Pd(NO_3)_2$, calcined at 500 °C in air and finally steam-aged at 800 °C for 6 h (90% O_2 + 10% H_2O). A reference steam-aged Pd/Al_2O_3 catalyst was also prepared for comparison.

2.2. Catalytic activity measurement

Catalytic activity tests were performed on both reduced and aged solids (250 mg of catalyst) by using a mixture consisting of CH_4 (1 vol.%), O_2 (4 vol.%) and N_2 balance with a total flow rate of 36 l/h. Catalytic activity cycle consisted of four steps: a heating ramp from 200 to 900 °C at 1 °C/min, a stand-by at 900 °C for 1 h, a cooling down to 300 °C at 5 °C/min and a second heating ramp up to 900 °C.

Measurements were also performed with catalysts diluted 40-fold with the support leading to a final GHSV of ca. $3 \times 10^6\ h^{-1}$.

2.3. X-ray diffraction

X-ray diffraction (XRD) patterns were obtained with a Siemens D500 spectrometer using a Cu anticathode and the Ni-filtered Kα at 1.5406 Å. The diffraction lines were recorded from $2\theta = 3^\circ$ to 70° and digitized every 0.02 values via an interface linked to a microcomputer. Data were compared to the JCPDS files.

2.4. BET area

The specific surface areas were measured by the BET method on a laboratory made apparatus after outgassing at 300 °C for 2 h under vacuum (10^{-2} Pa).

2.5. Diffuse reflectance spectroscopy

Diffuse reflectance spectroscopy (DRS) was performed at room temperature on a Perkin-Elmer Lambda 950 equipped with a 150 mm integrating sphere using Spectralon™ as reference. Solids as powder were put in a Spectralon™ sample holder equipped with a quartz window. Spectra were retrieved as ASCII files and transformed into Kubelka–Munk function F(R) analogous to absorbance for solids.

2.6. Oxygen thermoprogrammed desorption

PdO stability was studied by thermoprogrammed desorption (TPD) of oxygen. Samples were pretreated as follows. One hundred milligram catalyst was put in a quartz microreactor between two quartz wool layers. Solid was contacted with pure oxygen from room temperature up to 400 °C for 0.5 h with a ramp of 10 °C/min. Sample was then cooled down in He. Desorption of oxygen in He was recorded by using a PFEIFFER OMNISTAR quadrupole mass spectrometer from rt up to 1000 °C (linear heating ramp of 20 °C/min).

3. Results and discussion

3.1. Support

ICP chemical analysis confirmed that the composition corresponding to $Al_{18}B_4O_{33}$ was obtained. X-ray diffraction revealed that the solid calcined at 1100 °C was single phased with the $Al_{18}B_4O_{33}$ structure (JCPDS file 32-0003). The BET area value was of $18 \pm 2\ m^2/g$.

3.2. Catalytic activity

As it might be expected, the $Al_{18}B_4O_{33}$ prepared sample was almost inactive (10% conversion at 900 °C) compared to alumina [17].

For aged $Pd/Al_{18}B_4O_{33}$ catalyst, a rather low activity ($T_{50} = 595$ °C) was observed with respect to conventional palladium based catalysts (Fig. 1). At ca. 700 °C, a slight deactivation was observed (Fig. 1A). Upon the second heating ramp, the catalyst became highly active (Fig. 1B) showing a T_{50} of 370 °C, i.e. a decrease of more than 200 °C. The drop of conversion at 700 °C, previously, observed during the first heating ramp is no more observed. A slight decrease of conversion occurred at ca. 810 °C (100–95% conversion).

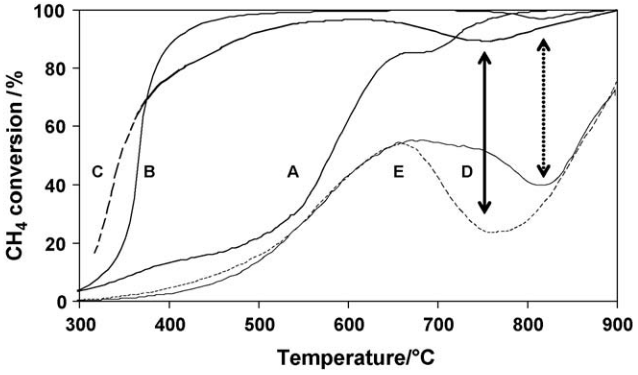

Fig. 1. Catalytic activity of aged palladium based catalysts: (A) $Pd/Al_{18}B_4O_{33}$ before test, (B) $Pd/Al_{18}B_4O_{33}$ after test, (C) Pd/Al_2O_3, (D) diluted $Pd/Al_{18}B_4O_{33}$ and (E) diluted Pd/Al_2O_3. Solid and dotted arrows indicate oxygen loss and reduced activity for Pd/Al_2O_3 and $Pd/Al_{18}B_4O_{33}$, respectively.

In order to better observe the activity drop at high temperature, a high GHSV has been used to measure the catalytic activity during the second heating ramp. A comparison with Pd/Al_2O_3 catalyst was made (Fig. 1C). Dilutions were operated with the respective supports. Drops of activity were clearly evidenced (Fig. 1D and E). For Pd/Al_2O_3, the drop of activity at about 750 °C can be attributed to the decomposition of PdO into metallic palladium, the latter being less active than the oxide [18]. In the case of Pd/$Al_{18}B_4O_{33}$, this drop of activity is observed at higher temperatures (ca. 820 °C). This could be tentatively ascribed to a stabilised form of PdO on $Al_{18}B_4O_{33}$. This form of PdO in interaction with the support would decompose into metallic palladium at higher temperature.

PdO on Al_2O_3 exhibits a high activity at low temperature. Interestingly, Pd/$Al_{18}B_4O_{33}$ after the first heating ramp under reactants is almost as active as PdO/Al_2O_3 in the low temperature region. In order to better understand the catalytic behaviour of Pd/$Al_{18}B_4O_{33}$ in the CH_4 combustion, we tried to identify and characterize the different oxide species responsible for the activity.

3.3. Thermo programmed desorption of oxygen

Three catalysts were tested: aged Pd/$Al_{18}B_4O_{33}$ before and after test and aged Pd/Al_2O_3 for comparison. For Pd/Al_2O_3, TPD profile showed only one maximum at 780 °C (Fig. 2A), indicating the presence of one kind of PdO species. For aged Pd/$Al_{18}B_4O_{33}$, catalyst before test the profile is somehow different (Fig. 2B). Three peaks of different intensities, respectively at 700, 760 and 860 °C can be distinguished. The same catalyst submitted to catalytic testing up to 900 °C exhibited a TPD profile with three peaks at, respectively 650, 850 and 900 °C.

From Figs. 2B and C, we may suggest the existence of three major kinds of palladium species on $Al_{18}B_4O_{33}$: type I species easily reducible (max at $T < 700$ °C), type II species with intermediate stability (max at ca. 750 °C) and type III species highly stable (max at $T > 800$ °C). Before catalytic testing, Pd/$Al_{18}B_4O_{33}$ mainly contains type II species, the amount of this species is comparable to the amount of PdO species in the Pd/Al_2O_3 sample. In addition, these species seem to exhibit the same properties of oxygen mobility as Pd/Al_2O_3. However, the low activity of this sample suggests that type II species are weakly active in CH_4 combustion compare to PdO supported on Al_2O_3.

After catalytic testing, the number of type II species decreased drastically with simultaneous appearance of types I and III species. These new species are thought to be responsible for the improvement of the catalytic activity compared to that measured on the aged catalyst. Type I species would be responsible for the catalytic activity in the low temperature region, while the presence of highly stable type III species would explain the shift of the conversion drop at higher temperature. The stability of type III species would result from a strong interaction with support.

3.4. Diffuse reflectance spectroscopy

DRS has been used in order to characterize Pd/$Al_{18}B_4O_{33}$ catalysts before and after test. The spectrum of bulk PdO prepared by decomposition of $Pd(NO_3)_2$ (500 °C in O_2) is shown in Fig. 3A. Two absorption bands at 360 and 430 nm are observed while no absorption in the near infrared range occurred. These bands are characteristic of Pd^{2+} ions in square planar coordination state [19]. PdO is a "p" semiconductor [20] and band gap energy E_g may be obtained from absorption edge by measuring the intercept of the two lines noted as "x" and "y" (Fig. 3A). A value of 2.08 eV (597 nm) is measured in accordance with literature data. For Pd/$Al_{18}B_4O_{33}$, before and after test the bands characteristics of bulk PdO are still observed. For the sample before test, the E_g value slightly increases with respect to bulk PdO (2.11 eV, 594 nm). This would indicate only a slight interaction with the support. After catalytic testing up to 900 °C, the significant increase of the E_g value (2.22 eV, 563 nm) is consistent with the existence of less semiconductor and more stable PdO species. These more stable species would correspond to the type III species evidenced by TPD experiments. Moreover, by comparison of band intensities in the UV range, absorption bands have been decreased by ca. 20%, suggesting the partial

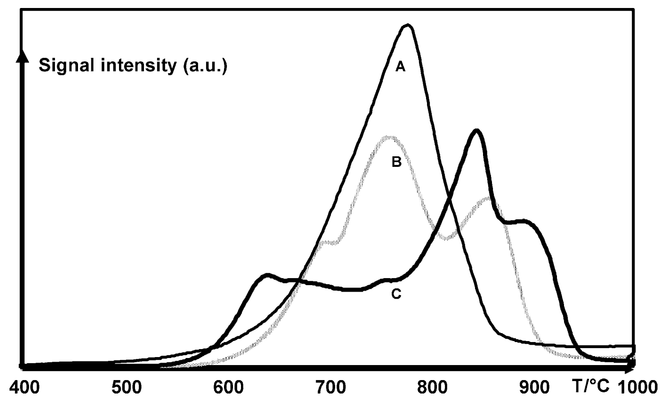

Fig. 2. Thermal desorption of oxygen from supported PdO: (A) aged Pd/Al_2O_3, (B) aged Pd/$Al_{18}B_4O_{33}$ catalyst before test and (C) aged Pd/$Al_{18}B_4O_{33}$ catalyst after test.

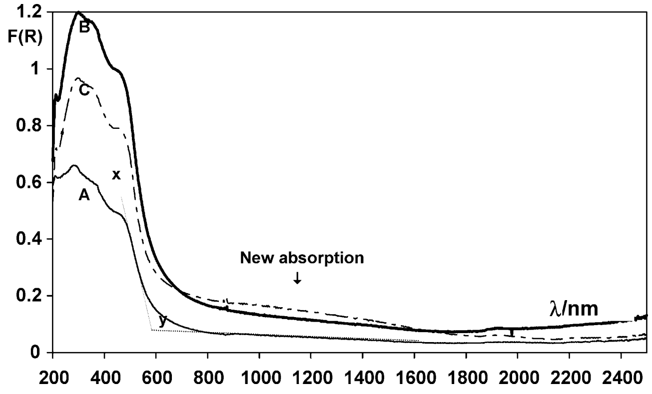

Fig. 3. Diffuse reflectance spectroscopy of Pd/$Al_{18}B_4O_{33}$ catalyst. (A) Bulk PdO: dotted lines "x" and "y" intercept at lambda corresponding to E_g, (B) aged catalyst before test and (C) aged catalyst after test: arrow indicates new absorption in the near infrared range.

transformation of PdO into other palladium oxide species of structure different from square planar. The existence of trigonal five coordinate sites has been shown in aluminium borate [15]. Such sites when located at the surface could be responsible for the presence of new palladium oxide species of lower symmetry. In such case, crystal field stabilisation energy is lowered, resulting in less stable Pd complexes and consequently more labile oxygen species. The existence of these highly labile oxygen species is in agreement with TPD results showing type I species of low stability. The local formation of surface mixed oxide species might also be proposed.

4. Conclusion

A new efficient $Al_{18}B_4O_{33}$ oxide was prepared as a support for palladium resulting in a fairly highly active catalyst in CH_4 combustion. Pd/$Al_{18}B_4O_{33}$ strongly activates under reaction mixture, which leads to a catalytic activity comparable to Pd/Al_2O_3 at low temperature. Moreover, this catalyst shows a much higher stability than Pd/Al_2O_3 in the high temperature region. This is attributed to the formation of new stabilised PdO species due to a strong interaction with the support, consistently with TPD and DRS data.

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