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Influence of the solid state properties of Pd/MOx (M = Ti, Al) catalysts in catalytic combustion of methane

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Abstract

The performance of Pd supported on alumina or titania, prepared by impregnation or sol–gel, for catalytic combustion of methane is studied. The addition of the Pd precursor after gelification of alumina has a beneficial effect on the catalytic properties of the catalysts. The better activity of the alumina catalysts is related to the high dispersion of the palladium particles, the low crystallite size and the high specific surface area. The catalytic activity of titania-based catalysts was only slightly affected by the preparation procedure. The addition of CO_2 during the oxidation of methane promotes oxidation for the titania-based catalysts.

Keywords: Titania; Sol–gel; Catalysts

1. Introduction

Catalytic combustion of methane (CCM) is a promising technology for a high energy yield, especially considering environmental impact [1,2]. Although a literature search shows that supported palladium catalysts are very active for deep oxidation of methane [1,3–5] and that many different palladium catalysts are being investigated [6,7], more active materials are still required for complete catalytic combustion in gas turbines. The performance of these catalysts has been related to the preparation procedure and to the nature of the support itself [8,9].

The main goal of this work is to compare the performance of Pd supported on different supports (alumina, titania) in the total oxidation of methane using two preparation methods (impregnation and sol–gel), and to relate the catalytic activity with the solid state properties of catalysts. We also studied the influence of CO_2 as co-feeding on catalytic performances.

2. Experimental

2.1. *Catalyst preparation: the catalysts were prepared with 2 wt.% Pd content*

2.1.1. *Impregnation, Pd/M(I), (M = Ti, Al)*

γ-Al_2O_3 and TiO_2 were impregnated with an aqueous solution of palladium tetraamine chloride. The pH of the solution was adjusted by ammonia addition to values of 10.6 and 8.6 when supported on alumina or titania, respectively. The suspension was stirred for 1 h at room temperature, the solvent was gently removed in a rotary evaporator at 45 °C, and the samples were finally dried in air at 100 °C for 12 h.

2.1.2. *Sol–gel*

Two methods were followed: (i) for Pd/M(SG), (M = Ti, Al) the palladium precursor was added to the medium before the gel formation: a mixture of aluminum *sec*-butoxide and *sec*-butanol or titanium tetraisopropoxide and isopropanol for alumina- or titania-based catalysts, respectively, was stirred for 20 min, and a solution of palladium acetylacetonate in acetone was then added. Afterwards, acetic acid glacial was added under vigorous stirring. The gel was dried in vacuum at 70 °C for 24 h and then the solid was calcined in oxygen flow at

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250 °C for 30 min and at 500 °C for a further 30 min (5 °C min^{-1}). (ii) For M(SG)Pd, (M = Ti, Al) the same aluminum and titanium precursors and solvents were used, but the support gel was formed prior to addition of the palladium precursor. The same experimental conditions as those of Pd/M(SG) solids were used. Reduction of I and SG catalysts was carried out in a 5% H_2–N_2 flow at 400 °C for 3 h. Finally, the solids were calcined at 600 °C for 3 h in air.

2.2. Catalytic tests were performed in a conventional fixed-bed micro-reactor (8 mm i.d.)

The space velocity was set to 18.75×10^{-2} m^3 g^{-1} h^{-1} using 320 mg (100 < dp < 315 μm) of catalyst. Two series of tests were performed: (i) in the absence of CO_2 ($CH_4/O_2/He$ = 1/10/89, v/v/v/v) and (ii) in the presence of 3% CO_2 in the gaseous reactants feed ($CH_4/O_2/CO_2/He$ = 1/10/3/86, v/v/v). When reporting the activity data, T_{MM} stands for the temperature necessary to reach MM% of methane conversion.

3. Characterization

The BET specific surface area was determined from nitrogen (Air Liquide) adsorption at −196 °C in a Micromeritics FlowSorb II 2300 instrument. The PXRD patterns were recorded on a Siemens D500 diffractometer using Cu Kα radiation (λ = 1.5418 Å); identification of the phases was achieved by using the JCPDS data base, and the average crystallite sizes were estimated using the Scherrer equation (instrumental line broadening $2\theta = 0.23°$) for which selected diffraction peaks were fitted by a Pearson-type profile function. XPS analysis was performed at room temperature with a photoelectron spectrometer SSI X-probe (SSX-100/206) from Surface Science Instrument of Fisons at a residual pressure of 5×10^{-9} Torr and using a monochromatic Al Kα (1486.6 eV) radiation (10 kV, 22 mA). The electron flood gun was adjusted at 6 eV by placing a nickel grid 3.0 μm above the sample and the pass energy for the analyzer was set at 50 eV. The spot size was 1000 μm in diameter, corresponding to a FWHM of 1.1 eV for the Au $4f_{7/2}$ band. Binding energy (BE) values were referred to the C 1s peak at 284.8 eV. The atomic concentration ratio was calculated by correcting the recorded intensities with the theoretical sensitivity factors based on Scofield cross sections. Peak decomposition was performed using 85% Gaussian and 15% Lorentzian type and a Shirley non-linear sigmoid-type baseline. The following peak intensities were used: Pd 3d, Ti 2p, Al 2p and O 1s. Palladium dispersion was determined by CO chemisorption in a Micromeritics Pulse Chemisorb 2700 equipment. Samples were pretreated in flowing H_2 at 100 °C for 30 min and at 400 °C for 3 h. The solid was cooled down to room temperature in flowing He and then CO pulses were introduced.

4. Results

4.1. Catalytic results

The best catalytic performance for alumina-based catalysts was measured for Al(SG)Pd (Fig. 1). For titania-based catalysts, Pd/Ti(I) is slightly more active than Pd/Ti(SG) up to 415 °C, while Pd/Ti(SG) shows the highest conversion at higher temperatures (Fig. 2). A poor activity is found for the Ti(SG)Pd catalyst. Comparison of performances of both alumina- and titania-based catalysts shows that Al(SG)Pd is the best catalyst at any temperature, while Ti(SG)Pd is the poorest material. At low temperatures, titania-based (Pd/Ti(I) and Pd/Ti(SG)) are more active than alumina-based catalysts (ca. T_{10} = 267 °C and T_{30} = 325 °C for Pd/Ti(I) versus T_{10} = 303 °C and T_{30} = 340 °C for Pd/Al(I); and T_{10} = 270 °C and T_{30} = 340 °C for Pd/Ti(SG) versus T_{10} = 315 °C and T_{30} = 350 °C for Pd/Al(SG)). The addition of 3% vol. CO_2 in the feed (Table 1) has a positive role on Pd/Ti(I) and Pd/Ti(SG) (T_{50} = 340 °C and 370 °C, respectively, with CO_2 versus T_{50} = 381 and 390 °C without CO_2) and to a lesser extent on Pd/Al(SG) (T_{50} = 360 °C with CO_2 versus T_{50} = 375 °C without CO_2). For Pd/Al(I), performances are unchanged.

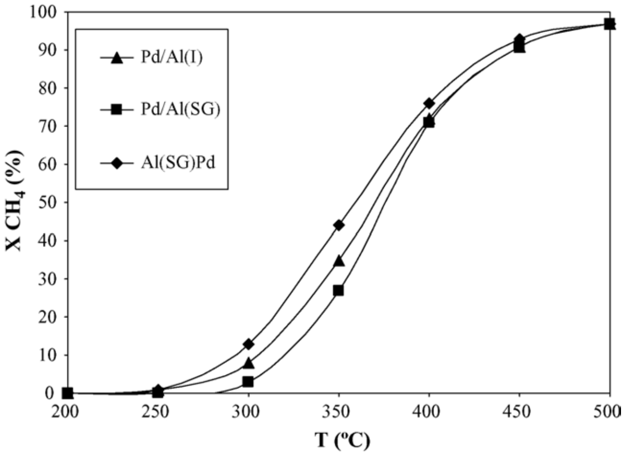

Fig. 1. CH_4 conversion as a function of temperature on alumina-based catalysts, prepared by impregnation (Pd/Al(I)) and via sol–gel (Pd/Al(SG) and Al(SG)Pd).

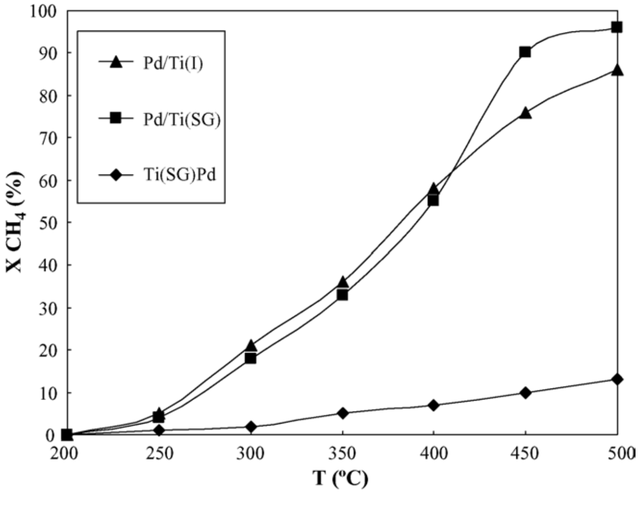

Fig. 2. CH_4 conversion as a function of temperature on titania-based catalysts, prepared by impregnation (Pd/Ti(I)) and via sol–gel (Pd/Ti(SG) and Ti(SG)Pd).

Table 1

Comparison of the temperature necessary to get 10, 30 and 50% of CH_4 conversion (T_{10}, T_{30} and T_{50}) on Pd alumina- and Pd titania-based catalysts in the absence of CO_2 and T_{50} by adding 3% CO_2 into the reactants feeds

Catalyst	Without CO_2			With CO_2
	T_{10}	T_{30}	T_{50}	T_{50}
Pd/Al(I)	303	340	368	363
Pd/Al(SG)	315	350	375	360
Pd/Ti(I)	267	325	381	340
Pd/Ti(SG)	270	340	390	370

4.2. Characterization results

4.2.1. Alumina-based catalysts

PXRD patterns of alumina-based catalysts showed formation of palladium oxide – (1 0 1) planes at 2.64 Å and (1 1 2) planes at 1.67 Å – while alumina was amorphous. These catalysts show higher surface areas than the titania-based ones. Compared to those prepared by sol–gel, the impregnated catalysts showed lower S_{BET} values (40–60%) (Table 2), but S_{BET} remained unchanged after reaction for both types of catalysts. Nanometric PdO particles are observed in all alumina-based samples. Since the crystallite size is higher for Pd/Al(I), the best Pd dispersion was found for Al(SG)Pd. Regarding XPS results, the O 1s line spectra showed only one component at 531.1 eV, which coincides with the position of oxygen bonded to Al in γ-Al_2O_3. The binding energy of Pd $3d_{5/2}$ (Table 2) is in agreement with Pd^{2+} species in PdO. The Pd/Al atomic ratio was similar for the three samples. Similar XPS results are observed for fresh and used samples.

4.2.2. Titania-based catalysts

The diffraction lines of both palladium oxide and titania were detected in the PXRD patterns – (1 0 1) planes at 3.52 Å (anatase) and (1 0 0) planes at 3.26 Å – with rutile contents ranging from 20% for Pd/Ti(I) to 5% for Pd/Ti(SG) and Ti(SG)Pd). No differences in the S_{BET} values were found between samples Pd/Ti(I) and Pd/Ti(SG), and Ti(SG)Pd showed a very low surface area. The PdO crystallite sizes were similar for Pd/Ti(I) and Pd/Ti(SG), and it was higher for Ti(SG)Pd. The XPS results for titania-based catalysts are shown in Table 2. The O 1s peak was decomposed in two peaks: the low BE, centered at 529.7 eV, is due to oxygen linked to Ti and the high BE at 531.7 eV is probably due to oxygen linked to C species, like C–O=C. The values of BE Pd $3d_{5/2}$ are typical of Pd^{2+} in PdO (Table 2). The lowest (Pd/Ti) atomic ratio obtained for Ti(SG)Pd indicates that Pd agglomeration is more pronounced on this sample, as compared to Pd/Ti(I) and Pd/Ti(SG). XPS results are similar for the samples after the catalytic test.

5. Discussion

5.1. Alumina-based catalysts

Activity measurements show that the catalytic performance of catalysts depends on the preparation procedure. The best performance found for Al(SG)Pd could be attributed to the higher Pd dispersion, which can itself be related to the formation of PdO on the alumina surface (and not inside the alumina particle), since alumina gelification takes place before the addition of the palladium precursor. Moreover, the sol–gel method seems to favour the increase of the specific surface area as well, as the specific surface areas of Pd/Al(SG) and Al(SG)Pd are higher than that of Pd/Al(I). The high specific surface area could alternatively be explained by the high surface area developed by the PdO particles (high dispersion and small crystallite size). A higher catalytic activity is observed for samples showing a high specific surface area and high dispersion. In addition, introduction of $Pd(acac)_2$ during the first step of the sol–gel catalyst preparation seems to have a detrimental effect on the catalyst performance.

5.2. Titania-based catalysts

The low activity found for Ti(SG)Pd might be due to the sintering of the solid, which gives a sharp increase of PdO crystallite size and a very low dispersion, as also concluded from the Pd/Ti XPS atomic ratios. Pd/Ti(I) and Pd/Ti(SG) show a similar catalytic activity up to 415 °C. The increase in methane conversion for Pd/Ti(SG) above 415 °C could be attributed to the lower amount of palladium exposed on the surface (low Pd/Ti XPS ratio) and probably to the different anatase/rutile ratio. In other words, both the support and dispersion degree play an important role in the conversion at high temperature.

Table 2

Specific surface area, metal dispersion, crystallite size and XPS results of Pd-alumina and Pd-titania-based catalysts

Catalyst	S_{BET} ($m^2\ g^{-1}$)	Pd dispersion (D%)	Crystallite size[a] (nm)			$(Pd/M)_{ESCA} \times 10^4$	BE Pd $3d_{5/2}$ (eV)
			PdO	Anatase	Rutile		
Pd/Al(I)	57	10	16	–	–	90	336.0
Pd/Al(SG)	92	10	6	–	–	95	336.7
Al(SG)Pd	130	16	7	–	–	90	336.5
Pd/Ti(I)	42	6	15	19	23	360	335.9
Pd/Ti(SG)	42	5	14	22	20	280	336.1
Ti(SG)Pd	9	1	28	21	16	160	336.2

[a] Average crystallite size determined by X-ray diffraction line broadening.

5.3. Effect of CO_2

Catalytic combustion of methane is observed at lower temperatures in the presence of CO_2 in the feed than in its absence for titanium-containing sample. These results confirm previous data claiming that CO_2 is not inert in this reaction and that its influence depends on the nature of the support [9,10]. The use of a titanium-containing support seems to improve greatly the beneficial effect of CO_2. An explanation of the effect of CO_2 might be the formation of active oxygen species arising from dissociation of CO_2 molecules at the surface of the catalysts, which could either help CH_4 oxidation or improve the oxidation state of Pd, thus increasing the overall activity of the catalysts. In a previous work, dissociation of CO_2 was concluded from variations observed in the low energy components of the O 1s XPS peak (centered at around 529.5 eV) after catalytic combustion on Pd/Ce-Zr-O in presence of CO_2. After reaction in the presence of CO_2, the proportion of these low binding energies O 1s species seems to increase and it is thought to be the consequence of some CO_2 dissociation occurring at the surface of Pd/Ce-Zr-O catalysts [10,11]. The effective role of CO_2 depends on the nature of supports. Reducible supports seem to favour dissociation of CO_2 [12]. However, this is a tentative explanation which must be confirmed on titania based catalysts.

6. Conclusions

The catalytic activity of alumina- and titania-based catalysts for catalytic combustion of methane depends both on the nature of the support (alumina, titania) and on the preparation procedure (impregnation, sol–gel). The support effect is more clearly evidenced for the samples prepared by the sol–gel method, in which the support gel is formed prior to the addition of the palladium precursor. The best conversion is measured for the aluminium-containing sample, while the titanium-containing sample is the poorest material. The preparation method leads to modifications in the surface of the catalysts that affect their catalytic behaviour. Taking into account both effects, the different performances observed for the catalysts can be attributed to the variations of crystallite size, dispersion of palladium particles, and specific surface areas of the solids. CO_2 in the feed increases significantly the catalytic activity of titanium-containing sample.

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