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Surface modifications of γ-Al_2O_3, SiO_2 and SnO_2 supports by titania grafting and their influence in the catalytic combustion of methane

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Abstract

The influence of the Ti-grafting of γ-Al_2O_3, SiO_2 and SnO_2 over Pd-supported catalysts and the presence of CO_2 as co-feeding, in the catalytic combustion of methane, were investigated. Important modifications in the catalytic performances due to grafting of supports were observed. The grafting method leads to formation of titania nanoparticles on the support surface. The interaction between Ti and support, changes in the size of Pd particles, changes in the acidity of supports could explain the modifications in catalytic performances due to grafting. The catalytic performances depend on the nature of the support and are different when CO_2 is introduced in the feed. CO_2 could play an important role, increasing or inhibiting the catalytic performance.

Keywords: Ti-grafting; Catalytic combustion of methane; Pd-supported catalyst and CO_2 co-feeding

1. Introduction

The catalytic combustion of methane (CCM) is an effective way to use methane as an environment-friendly fuel. For CCM at low temperature, Pd-supported catalysts are largely recognized as the best catalytic systems. The nature of the supports plays an important role on the catalytic behaviour of Pd-supported catalysts.

In this work, the surface of different supports has been modified by Ti-grafting and the performance of the resultant catalysts has been evaluated. The supports were chosen in order to compare the Ti-grafting effect on supports having different properties. We have previously shown that CO_2 plays a powerful oxidant role maintaining the surface sites in a high and more active oxidation state [1] improving performances in CCM [2]. The influence of CO_2 as co-feeding, which it is expected to depend on the nature of support, was also studied.

2. Experimental

2.1. Preparation of grafted support (Ti/MO_x ($M = Al, Si, Sn$))

The support (γ-Al_2O_3, SiO_2 and SnO_2) was added to a solution of isopropyl alcohol and titanium(IV) isopropoxide and evaporated in a rotavapor at 70 °C. The solid was dried at 110 °C/16 h and calcined at 500 °C/20 h. The TiO_2 amount corresponding to the theoretical monolayer was calculated taking into account that the Ti–O distance is equal to 0.154 nm, assuming a spherical hindrance for a TiO_2 unit and taking the above value as the radius of the projection of a TiO_2 unit on the support surface.

2.2. Preparation of catalysts (Pd/MO_x and Pd/Ti-MO_x)

The support was impregnated with a palladium containing solution by the wet impregnation method. The Pd-precursor used was $Pd(NH_3)_4Cl_2\cdot H_2O$ which was added in the suitable amount in order to obtain 2 wt.% metallic palladium catalyst. After stirring and evaporation, the solid was dried at 110 °C/16 h. The sample was heated up to 400 °C/1 h under O_2, then reduced under H_2 (5 vol.%)/N_2 for 3 h and finally calcined under air at 600 °C/3 h.

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2.3. Catalytic activity

A conventional fixed-bed micro-reactor operated at atmospheric pressure was used. Space velocity was 18.75×10^{-2} $m^3\,g^{-1}\,h^{-1}$ and kept constant in all experiments. One hundred sixty milligrams of the catalyst was used ($100\ \mu m < dp < 315\ \mu m$). Two kinds of tests were performed: (i) in the absence of CO_2 ($CH_4/O_2/He$ = 1/10/89 vol.) and (ii) in the presence of 3% CO_2 introduced in the feed ($CH_4/O_2/CO_2/He$ = 1/10/3/86 vol.). The T_X values are the temperatures necessary to reach X% of methane conversion. Some tests were performed twice in order to check their repeatability. These results indicate that the T_X values can be considered as significant when they are higher than 4 °C.

3. Characterisation

The BET specific surface was determined by means of a Micromeritics ASAP 2100 instrument using the adsorption of nitrogen at −196 °C. XRD patterns were recorded on a Siemens D5000 Diffractometer using the Kα radiation of Cu (λ = 1.5418 Å). The size of the PdO and TiO_2 crystallites was estimated from the most intense peak of the PdO (2θ = 33.89 (1 0 1)) and the anatase (2θ = 25.35 (1 0 1)) using the Debye–Scherrer formula. XPS spectra were performed with a photo- electron spectrometer SSI X-probe (SSX-100/206) from Surface Science Instrument of Fisons. A monochromatic Al anode (energy of Al Kα line 1486.6 eV) source, operating at 10 kV and 22 mA, was used. Binding energies were referenced to the C 1s peak (C–C, C–H) set at 284.8 eV. Zeta potential mea- surements were carried out in a PENKEM Zeta Meter. Apparent surface coverage (ASC) of TiO_2 values were obtained following [3]. The palladium metal dispersion was determined by CO-chemisorptions on a Micromeritics Pulse Chemisorb 2700 equipment. The ammonia chemisorptions experiments (TPD) were conducted at room temperature using a static volumetric apparatus Micromeritics Asap 2000 adsorption analyser.

4. Catalytic results

4.1. Pd/γ-Al_2O_3 and Pd/Ti-Al_2O_3 catalyst

Both catalysts present high performances. Pd/Ti-γ-Al_2O_3 is more active than with Pd/γ-Al_2O_3 (T_{50} = 377 °C for Pd/Ti-Al_2O_3 versus T_{50} = 386 °C). The addition of CO_2 in the feed decreases the activity of Pd/γ-Al_2O_3 catalyst at low reaction temperatures (T_{10} = 312 °C versus T_{10} = 321 °C with CO_2), whereas CO_2 does not influence the activity at higher temperatures (T_{50} = 383 °C versus T_{50} = 386 °C with CO_2). On the contrary, on Pd/Ti-γ-Al_2O_3 the activity was increased by CO_2 at any temperature (Fig. 1).

4.2. Pd/SiO_2 and Pd/Ti-SiO_2 catalysts

The conversion was greatly improved by Pd/Ti-SiO_2 in comparison with Pd/SiO_2 catalyst. The presence of CO_2 significantly inhibited the conversion on Pd/SiO_2. On the contrary, Pd/Ti-SiO_2 maintains its high performance (Fig. 2).

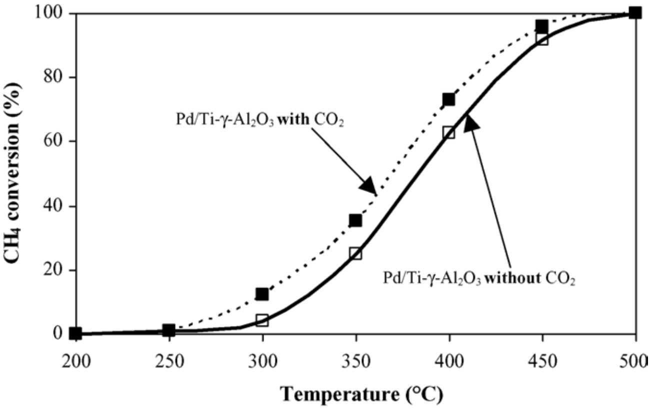

Fig. 1. CH_4 conversion as a function of temperature on Pd/$Al_{0.90}Ti_{0.10}$ (■, □) catalysts with (filled) and without (blank) addition of 3% of CO_2 in the feed.

4.3. Pd/SnO_2 and Pd/Ti-SnO_2 catalysts

Pd/Ti-SnO_2 catalyst was more active than Pd/SnO_2 (T_{50} = 369 °C versus T_{50} = 383 °C). The presence of CO_2 decreased the conversion of both catalysts although it was much more obvious on Pd/SnO_2, especially at lower reaction temperatures (T_{10} = 292 °C with CO_2 versus T_{10} = 303 °C).

5. Characterisation results

5.1. Pd/γ-Al_2O_3 and Pd/Ti-Al_2O_3 catalysts

The O 1s line for Ti-γ-Al_2O_3 exhibited only one component at 530.9 eV that coincides with the O 1s binding energy (BE) for pure γ-Al_2O_3. On Ti-γ-Al_2O_3, titanium presents a BE (Ti $2p_{3/2}$ = 458.7 eV) belonging to the Ti ions in the octahedral coordination typical for pure TiO_2. The fraction of the surface covered by TiO_2 is about 52% (ASC). XRD pattern showed the presence of nanometric anatase (28.2 nm) particles (2θ = 25.35 (1 0 1)) and γ-Al_2O_3 (2θ = 45.83); these particles remained

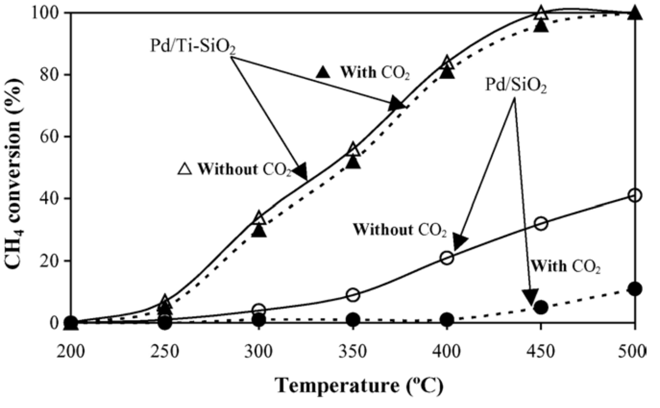

Fig. 2. CH_4 conversion as a function of temperature on Pd/SiO_2 (●, ○) and Pd/$Si_{0.85}Ti_{0.15}$ (▲, △) catalysts, both with (filled) and without (blank) addition of 3% of CO_2 in the feed.

Table 1
Physical–chemical properties of Ti-MO_x samples

Sample	TiO_2 (wt.%)	% ASC[a]	IEP	BET ($m^2 g^{-1}$)	Size of TiO_2 (nm)[b]	BE Ti $2p_{3/2}$ (eV)	Acidity (μmol NH_3 m^{-2})
Ti-γ-Al_2O_3	10	52	6.0	66.6	28.2	458.7	n.m.
Ti-SiO_2	13	79	3.9	98.1	25.6	459.2	n.m.
Ti-SnO_2	0.63	–	3.5	8.5	n.m.	458.8	n.m.
γ-Al_2O_3	–	–	8.2	64[c]	–	–	1.05
SiO_2	–	–	2.5	87[c]	–	–	0.19
SnO_2	–	–	4.7	7[c]	–	–	2.14

[a] Analysis of the present results in terms of ASC have been made, assuming that supported and unsupported TiO_2 exhibit the same IEP value of 4.6, and using the equation [3].

[b] Crystal size of TiO_2 determined by XRD. n.m.: not measured.

[c] Samples calcined for 3 h at 600 °C.

after palladium impregnation. XRD pattern of Pd-based catalysts clearly showed that palladium oxide ($2\theta = 33.89$ (1 0 1)) was formed. The Ti-grafting increased the total acidity (Table 1). CO-chemisorption results indicate that a better dispersion of Pd is achieved on Ti-γ-Al_2O_3. XPS results show that the Pd/Al atomic ratio is much higher for Pd/Ti-γ-Al_2O_3 (0.01) compared with Pd/γ-Al_2O_3 (0.005), indicating also a better dispersion of Pd on Ti-γ-Al_2O_3. These results are in agreement with the lower size of the PdO crystallites (17.2 nm on Ti-γ-Al_2O_3 versus 33.9 nm on γ-Al_2O_3) on Ti-γ-Al_2O_3. The palladium exhibits the same binding energy on both catalysts, which corresponds to Pd^{2+} in PdO. No relevant differences between the catalysts could be identified on the samples after test.

5.2. Pd/SiO_2 and Pd/Ti-SiO_2 catalysts

XPS results revealed that the O 1s line spectra for the Ti-SiO_2 sample shows two components. The largest peak coincides with the position of pure SiO_2 (532.7 eV), but the small one (530.4 eV) does not correspond to the expected value for pure TiO_2 (529.5 eV). This peak centred at 530.4 eV could be attributed to the oxygen in Ti–O–Si bonds [4,5]. In addition, the binding energy of Ti $2p_{3/2}$ for grafted sample is clearly higher than the one observed in pure titania (459.2 eV for Pd/Ti-SiO_2 versus 458 eV for TiO_2). The upward shift of Ti $2p_{3/2}$ value in the grafted sample can also confirm the formation of the Ti–O–Si bonds [5,6]. XRD results revealed that nanoparticles of titania (25.6 nm) were formed. Seventy-nine percent of silica was covered by TiO_2 particles (% ASC). Titania grafting sharply increased the total acidity (Table 2). All samples show a decrease of the surface area after deposition of Pd in comparison with the pure support. Pd/SiO_2 catalyst showed the highest loss in surface area. The XRD and XPS results indicated that palladium is only present as PdO. Pd supported on Ti-SiO_2 exhibits a higher BE (337 eV) than Pd on SiO_2 (336.3 eV), which indicates a stronger interaction between Pd and the grafted support. CO-chemisorption and XPS results show that Pd was better dispersed on the grafted support. When palladium is supported on silica, smaller PdO crystallites were formed (Table 1). All samples (with the only exception of Pd/SiO_2 after catalytic test performed with CO_2) presented identical XPS data before and after catalytic test. After reaction with CO_2, Pd/SiO_2 shows an enrichment in the component of the carbon peak located at around 287.5 eV, which corresponds to the reported binding energy of carbon bonded to oxygen (as C=O or C–O–O).

5.3. Pd/SnO_2 and Pd/Ti-SnO_2 catalysts

The titanium BE (Table 1) is attributed to the BE of pure TiO_2. The O 1s line spectra of Ti-SnO_2 showed two components (at 530.3 and 532.0 eV, respectively), both of them also appeared in the O 1s line spectra for pure SnO_2. The IEP of the Ti-SnO_2 support was lower than the corresponding one to the pure TiO_2 or to the pure SnO_2 leading to a value of ASC that is greater than 100%. As the sharp SnO_2 lines ($2\theta = 26.6$ (1 1 0) and $2\theta = 33.9$ (1 0 1)) were predominant, the diffraction lines

Table 2
Physical–chemical properties of Pd based catalysts

Sample	Size of PdO (nm)[a]	BET ($m^2 g^{-1}$)	BE Pd $3d_{5/2}$ (eV)	Pd dispersion[b]	Acidity (μmol NH_3 m^{-2})
Pd/γ-Al_2O_3	33.9	65.5	336.4	8.4	1.01
Pd/SiO_2	22.3	80.8	336.4	1.4	0.08
Pd/SnO_2	n.m.	5.1	336.0	–	2.06
Pd/Ti-γ-Al_2O_3	17.2	69.7	336.4	14.2	1.26
Pd/Ti-SiO_2	36.3	93.9	337.1	5.6	0.93
Pd/Ti-SnO_2	n.m.	8.1	336.1	–	1.86

[a] Size of PdO particles determined by XRD line broadening.

[b] Pd dispersion obtained by CO-chemisorptions.

from PdO and TiO_2 could not be observed. The surface area of Pd/SnO_2 remained unchanged after palladium deposition whereas a significant increase is displayed by $Pd/Ti\text{-}SnO_2$. Both samples present a similar acidity (Table 2). For these catalysts, the Pd dispersion could not be calculated because they did not adsorb CO [7]. The BE of Pd $3p_{5/2}$, for all catalysts, corresponds to PdO. XPS analysis corresponding to the samples after catalytic test were the same compared to the fresh catalysts, except for Pd/SnO_2 sample after test performed with CO_2 where a great increase in the component of the C 1s peak at 287.5 eV was detected.

6. Discussion

6.1. $Pd/\gamma\text{-}Al_2O_3$ and $Pd/Ti\text{-}\gamma\text{-}Al_2O_3$ catalysts

Titania nanoparticles were formed on the alumina surface. Alumina modified by titania ($Pd/Ti\text{-}\gamma\text{-}Al_2O_3$) presents the best performance at any temperature. This improvement could be attributed to the great increase of Pd dispersion and/or a higher acidity of the support on $Ti\text{-}\gamma\text{-}Al_2O_3$. CO_2 inhibits the conversion of $Pd/\gamma\text{-}Al_2O_3$ whereas an increase on the conversion of $Pd/Ti\text{-}\gamma\text{-}Al_2O_3$ is observed. These data confirm previous results about the role of CO_2 in CCM [2,8]. A possible explanation of the activating effect of CO_2 would be its dissociation, leading to active oxygen species which could help to oxidize directly CH_4 or to increase the oxidation state of Pd which are the actives sites for combustion [2]. Neither carbonates nor carbon deposition was detected by XPS after test with CO_2 on $Pd/\gamma\text{-}Al_2O_3$. However, carbonates formation has been observed in DRIFTs in situ experiments in the presence of CO_2 on a $Pd/\gamma\text{-}Al_2O_3$ catalyst [2,8]. Carbonates formation in our case cannot be completely excluded.

6.2. Pd/SiO_2 and $Pd/Ti\text{-}SiO_2$ catalysts

The upward shift of the Ti 2p could be attributed to the Ti–O–Si linkages [4,5]. The formation of Ti–O–Si bonds can significantly change the electronic structure of Ti species in grafted support, and increase the effective positive charge on the Ti due to decrease of the electron density around Ti species resulting from the greater electronegativity of Si [6]. In pure silica big palladium particles are formed; it is consistent with the loss of surface area in the Pd/SiO_2 catalyst and could explain, to a large extent, the low dispersion exhibited by palladium on silica. The interaction between Ti and Si, which could be responsible for the increase in the acidity, would greatly increase the palladium dispersion in $Pd/Ti\text{-}SiO_2$. In addition, there is a stronger interaction between Pd and $Ti\text{-}SiO_2$ support as it is deduced from the shift in the binding energy of Pd (Table 1). Therefore the improvement in the conversion displayed by $Pd/Ti\text{-}SiO_2$ could be due to the interaction Ti–Si, to the better Pd dispersion and also to the stronger interaction of Pd on the grafted support. In the presence of CO_2, Pd/SiO_2 catalyst was deactivated while $Pd/Ti\text{-}SiO_2$ catalyst kept its high performance. According to XPS results, C–O species were produced on Pd/SiO_2 in the presence of CO_2. These species could be responsible for the deactivation of Pd/SiO_2 catalyst in the presence of CO_2. Such species were not detected in the grafted catalyst. A possible explanation could come from the different surface properties of both supports (pure and grafted). Some molecules of CO_2 could dissociate on the grafted support, creating powerful oxidant O^* species which would be able to oxidize either some metallic palladium or directly C–O species improving $Pd/Ti\text{-}SiO_2$ activity. As discussed above, CO_2 plays a powerful oxidant role maintaining the surface sites in a high and more active oxidation state [1].

6.3. Pd/SnO_2 and $Pd/Ti\text{-}SnO_2$ catalysts

Pd/SnO_2 catalyst showed a high activity in spite of its small superficial area. The increase in the activity showed by the $Pd/Ti\text{-}SnO_2$ catalyst is probably due to the increase in the superficial area which could be related to a greater dispersion of the Pd and to a new structure associating Sn and Ti (IEP). The CO_2 presence for both catalysts did not seem to affect significantly its activity, although a slight inhibition could be suggested in the Pd/SnO_2 catalyst. This could arise from the deposition of some C–O species (increase of the component of the C 1s located at 287.5 eV) after reaction with CO_2, as it has been explained previously for silica-supported catalysts.

7. Conclusions

The grafting of titania leads to significant modifications in the surface of the supports ($\gamma\text{-}Al_2O_3$, SiO_2 and SnO_2), which affect their catalytic behaviour. TiO_2 nanoparticles can be found at the surface of the support and new structures associating titania with the support or with metals could be formed, depending on the support. In addition, the palladium particles size and the acidity of the support can be modified by grafting. The effect on the catalysts performance depends on the support and is different when CO_2 is introduced in the feed. CO_2 could play an important role increasing or inhibiting the catalytic performance. The effect of CO_2 depends also on the support used for Pd deposition.

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