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Rh/Ti–SiO_2 catalysts prepared by organic grafting: A novel class of catalysts towards hydrogen production by partial oxidation of methane

C. Mateos-Pedrero *, C. Cellier, P. Ruiz

Unité de Catalyse et Chimie des matériaux Divisés, Université Catholique de Louvain, Croix du Sud 2/17,
B-1348 Louvain-La-Neuve, Belgium

Abstract

The influence of grafting Ti over SiO_2 surface, the Ti loading and the catalytic performance of Rh supported on Ti–SiO_2 catalysts in the partial oxidation of methane have been studied. Ti-grafting led to modifications in the surface of the catalysts that affect significantly their catalytic behaviour. The grafting method gives rise to two different Ti-species: (i) titanium in the Ti–O–Si bonds; (ii) anatase nanoparticles on the support surface for the highest Ti amount. Ti-grafted catalysts led to a significant improvement in the activity, as well as in the selectivity towards H_2 and CO, related to bare supports (SiO_2 and TiO_2). The performance of such catalysts depends on the Ti loading. These positive effects could arise from the ability of titania to modify redox properties as well as rhodium dispersion. Results suggest guidelines for the design of very active and selective Rh-based catalysts in POM for producing hydrogen.

Keywords: Titanium grafting; Hydrogen production; Partial oxidation of methane; Redox properties; Rhodium dispersion

1. Introduction

Silica–titania represents an interesting class of materials, which have attracted much attention in the last decades. Such materials not only take advantage of both TiO_2 (a n-type semiconductor and an active catalytic support) and SiO_2 (high thermal stability and excellent mechanical strength), but also extend their applications thanks to the generation of new catalytic sites due to the interaction of TiO_2 with SiO_2 [1]. Many different preparation methods have been employed to synthesize titania–silica supported oxides, being the most widely used: impregnation [2–4], chemical vapour deposition [5] and precipitation [6]. Another method much less employed is the grafting of the supports by small amounts of titanium precursor. Some papers have recently dealt with the preparation of catalysts obtained by grafting metal alkoxides on surface hydroxy groups of different carriers. A group of papers describes grafting of vanadyl triisopropoxide on different oxides, such as ZrO_2, TiO_2 and SiO_2 to obtain catalysts with improved redox properties and desired dispersions [7,8]. Others describe the grafting of titanium alkoxides on silica [3,9] leading to a TiO_2-coated material with an extremely high dispersion which is useful as a catalytic support. Finally, a few papers deal with grafting alkoxides with the aim of modifying the acidity of a surface [10], by reacting tetraethoxysilane with the surface hydroxyls of alumina. TiO_2–SiO_2 supported oxides were prepared by grafting in liquid phase with organic or inorganic titania compound [11]. The authors [11] found that the morphology as well as the surface properties of the resulting solids largely depends on the preparation procedure. More recently, TiO_2–SiO_2 oxides were prepared by a multistep grafting of Titanium tetraisopropoxide on silica [12–14]. Clearly the choice of the preparation method used for synthesizing titania–silica catalysts, plays a crucial role in the properties of the resulting solids.

The partial oxidation of methane (POM) represents an attractive process for syngas formation. This process is likely to become more important in the future due to its thermodynamic advantages: (i) it is mildly exothermic; (ii) the H_2/CO ratio produced in stoichiometric POM is 2, which is ideal for

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* Corresponding author.
E-mail address: mateos@cata.ucl.ac.be (C. Mateos-Pedrero).

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downstream processes. The catalysts most widely used in POM are those based on noble metals and Ni-based catalysts. Among these, catalysts based on noble metals, particularly Rh, are preferred because they avoid the coke deposition, which is the main disadvantage of Ni supported catalysts. However, rhodium is more expensive, therefore Rh supported catalysts are usually prepared with low loading, ranging from 0.5 to 2 wt.% Rh. In this work, we focused our attention on silica–titania materials prepared by organic grafting used as supports for the synthesis of Rh-based catalysts, which represent a new class of catalysts (Rh/xTi–SiO_2), not reported until now, for H_2 production by the partial oxidation of methane.

2. Experimental

2.1. Catalysts preparation

The silica–titania supports were prepared by organic grafting of a silica support from Alfa Aesar 042737 (surface area = 100 m^2/g) with titanium(IV) tetraisopropoxide Ti $[OCH(CH_3)_2]_4$ (Aldrich pure grade) in isopropanol (Aldrich 99+%), following the same procedure as detailed in [15]. Grafted samples will be denoted as xTi–SiO_2, where x represents the TiO_2 amount corresponding to the theoretical monolayer (x = 13 wt.% TiO_2) or to the 0.25 theoretical monolayer (x = 3 wt.% TiO_2). 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 [15]. The supports (TiO_2, SiO_2 and xTi–SiO_2) were impregnated with Rh (0.8 wt.%) with an aqueous solution of $(NH_4)_3RhCl_6\cdot 3H_2O$ (Aldrich, 28 wt.% Rh), then dried overnight at 110 °C and calcined at 700 °C for 4 h in air.

2.2. Catalytic tests

The gaseous feed was composed of a mixture of 5 vol.% of CH_4 (Indugas, 99.5%) and 2.5 vol.% of O_2 (Indugas, 99.5%) diluted in nitrogen (Indugas, 99.9%) for a total flow of 100 ml/min. The amount of the catalyst was 100 mg (particle size between 200 and 215 μm). Before starting the reaction a pre-reductive pre-treatment was done using a pure H_2 flow (Indugas, 99.5%) for 3h at 600 °C (slope 10°/min). The catalytic activity was measured between 400 and 700 °C, and then the reactor was cooled down under the reaction conditions.

2.3. Characterisation

The BET surface area was measured through N_2 adsorption at liquid nitrogen temperature by using a Micromeritics TriStar 3000 instrument. XRD patterns were recorded on a Siemens D5000 Diffractometer using the Kα radiation of Cu (λ = 1.5418 Å). TiO_2 average crystallite size was estimated from X-ray diffraction line broadening using the Debye–Scherrer formula. XPS spectra were performed with a photoelectron 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 measurements were carried out in a PENKEM Zeta Meter. Apparent surface coverage (ASC) of TiO_2 values were obtained following [16]. The metallic dispersion was determined by H_2 chemisorption at room temperature, using a static volumetric apparatus Micromeritics ASAP 2010C adsorption analyser. NH_3 chemisorptions experiments (TPD) were conducted at room temperature using a static volumetric apparatus Micromeritics ASAP 2000 adsorption analyser. Pyridine adsorption spectra were recorded using a Bracker IFS 88 spectrometer after evacuation (7×10^{-5} Torr) for 1 h at room temperature, at 50, 100, 150, 200 and 300 °C, respectively.

3. Results

3.1. Catalytic activity

The modification of the SiO_2 surface by Ti grafting observed at 600 °C, mainly leads to (Fig. 1): (i) a significant enhancement in the CH_4 conversion; (ii) an increase in the yields of H_2 and CO, which is particularly marked for the highest Ti loading (Rh/13Ti–SiO_2); (iii) a decrease in the formation of CO_2 and H_2O. The selectivity towards the

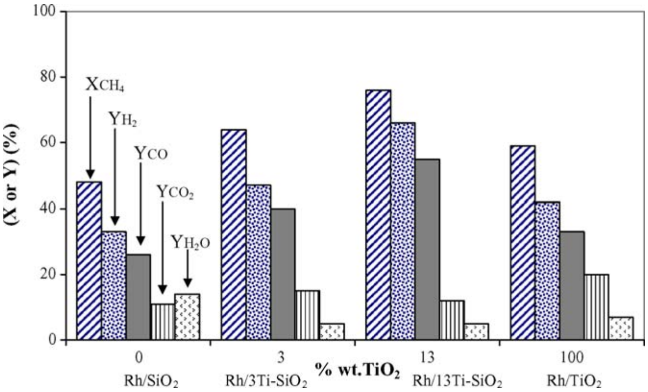


Fig. 1. CH_4 conversion, yields of H_2, CO, H_2O and CO_2 at 600 °C, as a function of the titanium loading in the catalysts.

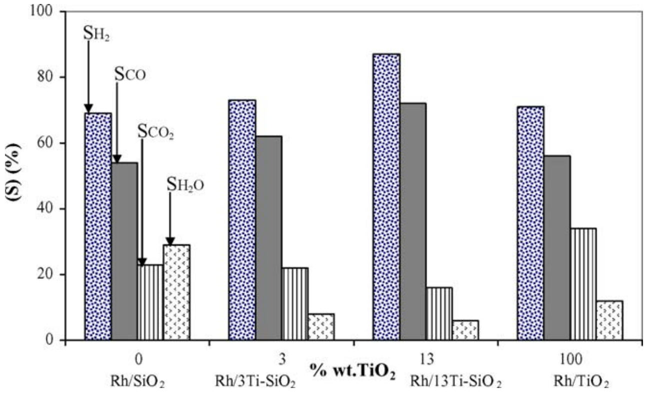


Fig. 2. Selectivity towards H_2, CO, H_2O and CO_2, at 600 °C as a function of the Ti loading in the catalysts.

Table 1
Summary of the physico-chemical properties of the modified supports and of Rh-supported catalysts

Sample	%ASC[a]	IEP	BET (m^2/g)		BE Ti $2p_{3/2}$ (eV)	Acidity (µmol NH_3/m^2)		d_{TiO_2}[b] (nm)
SiO_2[c]	–	2.5	87	88[d]	–	0.19	0.81[d]	–
3Ti–SiO_2	34	2.9	89	89[d]	458.9	0.57	0.74[d]	Amorphous
13Ti–SiO_2	79	3.9	98	96[d]	459.2	0.73	0.99[d]	19
TiO_2[c]	–	4.7	14	16[d]	458.0	2.14	1.97[d]	59

[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 [16].

[b] Average crystallite size determined from X-ray diffraction line broadening.

[c] After calcination at 700 °C for 4 h.

[d] After Rh impregnation.

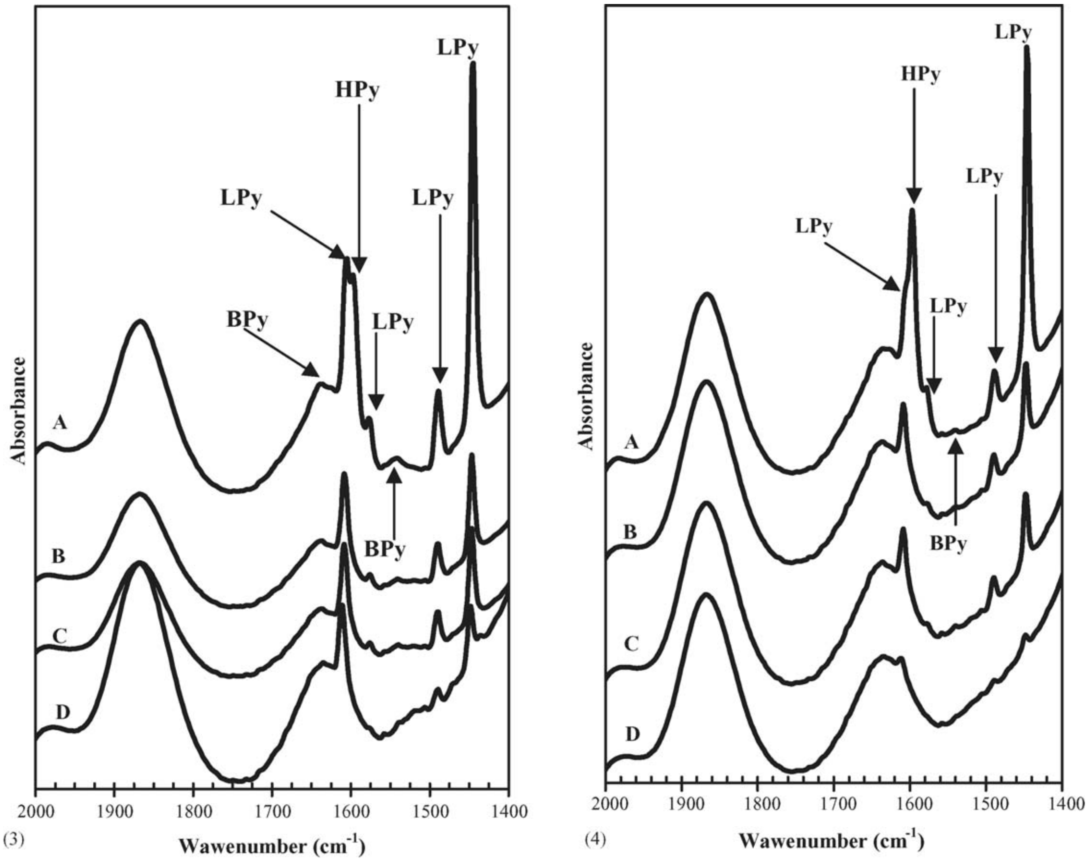
different products, at 600 °C, is depicted in Fig. 2. It can be seen that both H_2 and CO selectivities are higher for the grafted supports (xTi–SiO_2) than for the bare supports (SiO_2 and TiO_2). Data displayed in Fig. 2 show that the selectivity towards syngas is clearly dependent on the titanium amount. In fact, selectivity towards H_2 as well as CO is increasing with the TiO_2 content. It should be noticed that the catalyst with the highest titania content (Rh/13Ti–SiO_2) is by far the most H_2 selective among all catalysts tested. The H_2/CO ratio is very close to 2 from 550 to 700 °C, but at lower temperatures this ratio is quite bigger (close to 9), indicating that POM is not the only reaction involved.

3.1.1. Characterisation of the supports

ICP results indicate that all xTi–SiO_2 samples present an experimental TiO_2 percentage, which is similar to the theoretical one (Table 1). XRD analyses showed that SiO_2 remains unchanged after grafting with Ti. XRD patterns for 13Ti–SiO_2 showed the appearance of a very broad peak being characteristic of TiO_2 as anatase, whereas the 3Ti–SiO_2 sample was amorphous. As shown in Table 1 the ASC values increase with the TiO_2 content. Moreover, regarding the isoelectric point (IEP) values, we can observe that the catalysts obtained by grafting Ti on SiO_2, after drying and calcination, present a higher IEP than SiO_2, which increases with the Ti loading, approaching the value of pure TiO_2 (Table 1). According to the data derived from NH_3 chemisorption, SiO_2 used in this work exhibits very low acidity in contrast with the higher acidity displayed by TiO_2 (Table 1). For the grafted samples it is observed that the overall number of acid sites increases, on the one hand, after grafting with Ti and on the other hand with the titania amount (Table 1). The low wavenumber region of IR spectra of pyridine adsorbed on SiO_2 (not shown here) displays two bands located at 1445 and 1597 cm^{-1}; the first band is commonly attributed to pyridine adsorbed on Lewis acid sites (LPy) and the second one could be owing to pyridine H-bonded (HPy) on SiO_2 surface. Both bands disappeared after evacuation at 50 °C confirming the low acidity of SiO_2, as indicated earlier by NH_3 chemisorption. The IR spectra of pyridine adsorbed on TiO_2 only exhibits bands at 1603, 1573, 1488 and 1445 cm^{-1}, which are attributed to LPy species. Moreover, these Lewis acid sites are strong since pyridine is still adsorbed on TiO_2 surface, above 300 °C. The IR spectra of pyridine adsorbed on 13Ti–SiO_2 (Fig. 3) displays also the same four bands as pure TiO_2, being characteristic of pyridine coordinated to Lewis acid sites (denoted as LPy in Fig. 3). In addition, two weak bands at 1637 and 1537 cm^{-1}, which are assignable to pyridine coordinated to Brönsted acid sites (labelled as BPy in Fig. 3) were detected. Increasing the temperature up to 100 °C resulted in the disappearance of such species, revealing that they are not very stable against temperature. On the contrary, the stability of the LPy species to outgassing at 300 °C indicated that the Lewis acid sites formed are strong. The close similarity between the νCCN band structures of LPy species established on 13Ti–SiO_2 and 3Ti–SiO_2 at room temperature (Fig. 4) is noteworthy, although the band at 1604 cm^{-1} is something different. In fact, this band appears as a shoulder because of the presence of the most intense band at 1597 cm^{-1} (denoted as HPy in Fig. 4). However, the fact that the intensity of the band at 1537 cm^{-1} is very weak (labelled as BPy in Fig. 4) and the band at 1637 cm^{-1} was not detected, suggests that the Brönsted acid sites are in much lower ratio and are also very weak. Another relevant difference in the acidity of both samples is the strength of the acid sites formed. In the case of the 3Ti–SiO_2 sample all bands disappeared following outgassing at 300 °C (Fig. 4); in contrast, in the 13Ti–SiO_2 sample, the LPy species persisted against outgassing at the same temperature (Fig. 3). As far as XPS analysis is concerned, all the binding energies of titanium (Ti $2p_{3/2}$ = 458–459.2 eV) are in agreement with the reported binding energy of Ti^{4+} [17]. On the contrary, Si 2p binding energy for modified supports is about 0.6 eV lower in comparison with bare SiO_2. The XPS Ti $2p_{3/2}$ binding energy value for the grafted samples is clearly higher related to that in the bare TiO_2 (459.2 eV *versus* 458 eV). XPS spectrum for the 13Ti–SiO_2 sample reveals that the O 1s line presents 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 value for pure TiO_2 (529.5 eV).

3.1.2. Characterisation of the Rh-based catalysts

Compared to original supports, the surface area remains unchanged after impregnating rhodium for Rh/TiO_2 whereas it decreased slightly for the Rh/SiO_2 (Table 1). The surface area is not affected by Rh impregnation in the case of grafted catalysts. The deposition of rhodium brought about an increase of the acidity for catalysts containing silica and a decrease for Rh/TiO_2 catalyst. FTIR spectra for Rh/SiO_2 showed the same two bands



Figs. 3 and 4. Low-wavenumber IR spectra of pyridine adsorbed on 13Ti–SiO_2 (on the left, Fig. 3) and on 3Ti–SiO_2 (on the right, Fig. 4), respectively: (A) at room temperature; (B) after evacuation at 100 °C; (C) after evacuation at 200 °C; (D) after evacuation at 300 °C.

(1597 and 1445 cm^{-1}) as for bare silica, corresponding to the formation of LPy; but these bands are stronger than pure silica since they are observable up to 150 °C. This latter observation confirms the increase in the acidity showed by NH_3 chemisorption results (Table 1). The IR spectrum of pyridine adsorbed on Rh/TiO_2 exhibits the same four bands as for bare TiO_2, which are attributed to the formation of LPy species. As for pure TiO_2, these acid sites are strong. Two sharp bands at 1597 and 1445 cm^{-1} dominate the IR spectrum of the grafted catalysts. In addition, there is a broad band at around 1487 cm^{-1} and another weak feature at 1578 cm^{-1}. All of them are similar to those described for grafted supports and belong to LPy species but having lower intensity in comparison with supports before impregnating rhodium. In this case, Brönsted acid sites were not detected. As for the grafted supports, the Lewis acid sites formed on Rh/13Ti–SiO_2 are somewhat stronger than on Rh/3Ti–SiO_2. The dispersion seems not to be dependent on the surface area; in fact, all catalysts exhibit similar values (H_2 chemisorption), although results obtained by this technique must be interpreted with attention because of a strong metal–support interaction with titania could not be excluded [18]. XPS and XRD results of the samples (fresh, reduced or after reaction), provided some clues about the dispersion and the oxidation state of Rh. The Rh/Si atomic ratio does not change significantly either after reductive pre-treatment or after test and is largely lower than the theoretical value (Table 1). The XPS Rh/Ti ratio remains also constant, after reduction or reaction, and coincides with the theoretical one, indicating a higher Rh dispersion on TiO_2 than on SiO_2. XRD results confirm this observation. In fact, XRD patterns of the fresh Rh/SiO_2 reveal the presence of Rh_2O_3. The characteristic peaks of metallic rhodium are observed for Rh/SiO_2 after reduction or test. In the case of Rh/TiO_2 the diffraction lines from Rh_2O_3 and/or Rh could not be observed since the sharp TiO_2 lines were predominant, although after test and reaction a broadening of TiO_2 peaks seems to reveal the presence of some crystalline Rh species. These results suggest a higher dispersion of Rh on TiO_2 support. Ti-grafting improved the rhodium dispersion in comparison with Rh/SiO_2; moreover it is increasing with the Ti loading, as showed by XPS results. For fresh samples, a broad peak of Rh_2O_3 is observed on 3Ti–SiO_2 whereas only traces were detected on 13Ti–SiO_2. After reduction and test, a broad diffraction peak of metallic rhodium was observed. These results confirm the higher Rh dispersion on grafted samples related to bare silica. Rh/TiO_2 catalyst shows an important growth of anatase crystallites size accompanied by an increase of the intensity of rutile peaks, revealing the *rutilization* of the support. Grafted samples did not show any appreciable difference. For Rh on grafted supports, the XPS Rh/Ti + Si ratio is very close to the theoretical one (Table 2). For the Rh/13Ti–SiO_2 catalyst, a diminution of the XPS Rh/Ti + Si ratio was observed after reduction, and remained also after test. This effect would be presumably related to the Rh dispersion. Concerning the oxidation state of Rh, it can be noticed that the binding energy of Rh $3d_3$: (i) for fresh catalysts, is about 308.8 eV which

Table 2
Physico-chemical properties of the Rh-supported catalysts

Sample	Crystal phase	$(Rh/M)_{XPS}$ ($\times 10^4$)	Bulk atomic ratios[a] ($\times 10^4$)	XPS BE Rh $3d_{5/2}$ (eV)	D[b] (%)
Rh/TiO_2					
Catalyst before test	Anatase/rutile	900	900	309.0	17
Reduced catalyst	Anatase/rutile	871	–	306.9	n.m.
Catalyst after test	Anatase/rutile	900	–	307.6	n.m.
Rh/SiO_2					
Catalyst before test	Rh_2O_3	200	600	308.5	16
Reduced catalyst	Rh^0	100	–	306.9	n.m.
Catalyst after test	Rh^0	100	–	307.7	n.m.
$Rh/13Ti–SiO_2$					
Catalyst before test	Anatase/Rh_2O_3 (traces)	63	67	308.9	15
Reduced catalyst	Anatase/Rh^0	36	–	307.0	n.m.
Catalyst after test	Anatase/Rh^0	37	–	307.0	n.m.
$Rh/3Ti–SiO_2$					
Catalyst before test	Rh_2O_3 (traces)	60	65	308.8	14
Reduced catalyst	Rh^0	55	–	307.1	n.m.
Catalyst after test	Rh^0	58	–	308.3	n.m.

M = Ti, Si for Rh/TiO_2 and Rh/SiO_2, and (Ti + Si) for the grafted catalysts; n.m.: not measured.

[a] Calculated theoretically.

[b] Rh dispersion obtained by H_2 chemisorption.

corresponds to the reported value for Rh^{3+} in Rh_2O_3; (ii) for reduced catalysts, is shifted to lower binding energy values at around 307 eV, which is attributed to Rh^0; (iii) for catalyst after test, is shifted to higher values related to reduced samples, indicating that reoxidation is occurring during the reaction. However, the reoxidation depends on the support, indeed Rh is partially reoxidized on TiO_2 and $3Ti–SiO_2$ whereas it is fully oxidized over SiO_2. It is important to remark that Rh did not show any noticeable reoxidation when supported on $13Ti–SiO_2$.

4. Discussion

4.1. Titania dispersion

For the grafted samples there is an increase in the dispersion with the TiO_2 content. The same conclusions are suggested by zeta potential measurements, where the ASC values are increasing when the titania content is growing from 3 to 13 wt.%. These results together with XRD, seems to confirm that: (i) the titania dispersion increases with the TiO_2 loading; (ii) crystallites are formed at the expense of the dispersed titania as the content is increased. As increases the titania loading, apparently two phenomena are occurring: on the one hand the increase of the titania dispersion, on the other hand the formation of titania crystallites. For the sample with the lowest TiO_2 loading ($3Ti–SiO_2$), no crystallites of titania are formed. For the highest TiO_2 loading ($13Ti–SiO_2$) the increased dispersion process is favoured, which leads also to the formation of small titania crystallites.

4.2. Titania–silica interaction

XPS analysis shows that a significant difference of about 1.2 eV in the binding energy of Ti with respect to the TiO_2 bulk oxide (anatase) was observed for the organically grafted samples. This upward shift of the Ti 2p could be attributed to the Ti–O–Si linkages [1,10]. 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. These changes in the coordination of titanium also induce changes on the O 1s photoelectron peak associated to Ti. Since Ti is more electropositive than Si, the core electron-binding energy of the oxygen atom is reduced when a Ti–O–Si bond replaces a Si–O–Si bond. The Ti–O bond would be more ionic in character, thus making the oxygen atom more negative, explaining the shift in the O 1s photoelectron peak.

4.3. Acidity

The number of acid sites per unit surface area was significantly larger for titania than silica which did not possess a detectable number of acid sites (NH_3 chemisorption and pyridine adsorption). The acidic properties of xTi–SiO_2 samples are different from that of either pure TiO_2 or pure SiO_2, which is in good agreement with results reported in the literature [1,17,19]. The main conclusions coming from acidity studies are: (i) the overall number of acid sites increased with the titania content (NH_3 chemisorption); (ii) the strength and the nature of acid sites depends on titania content as well as on the presence of Ti–O–Si bonds; actually, stronger Lewis acid sites are present in the support containing the highest TiO_2 loading ($13Ti–SiO_2$) in comparison with the $3Ti–SiO_2$ sample. The $13Ti–SiO_2$ sample exhibited also a more appreciable Brönsted acidity related to that of the $3Ti–SiO_2$ sample (IR). The same catalysts showed an increase of the IEP values with the Ti loaded, revealing a more basic character than pure SiO_2, which seems to suggest that basic sites of comparable strength to those observed in pure TiO_2

could be present on the surface of Ti-grafted catalysts. Several hypotheses have been proposed in order to explain the acidity in TiO_2–SiO_2 systems [20–22], and despite the widely accepted fact that the Brönsted acid sites are associated with the Ti–O–Si bridges, the generation of such acid sites is still open to question.

4.4. Catalytic performance

Concerning pure oxides, Rh/TiO_2 is slightly more active than Rh/SiO_2. As previously mentioned, Rh is highly dispersed and also more reduced (a larger amount of reduced Rh is detected by XPS, on TiO_2 than on SiO_2), on TiO_2. These properties remained even after reduction or reaction. It suggests that titania gives to rhodium the resistibility against reoxidation and/or sintering occurring during reduction and/or reaction (XPS). Therefore, the higher activity showed by this catalyst (related to Rh/SiO_2), is probably owing to the capability of TiO_2 for maintaining Rh in a highly dispersed and reduced state during reaction. It is noteworthy to remark that Ti-grafting significantly enhanced the catalytic activity in comparison with pure oxides (TiO_2 and SiO_2). The correlation between the oxidation state and catalytic activity was common to all catalysts. In fact, the order of resistibility against oxidation corresponds to $13Ti–SiO_2 > 3Ti–SiO_2 > TiO_2 > SiO_2$, which coincides also with the order of increasing activity. It suggests that the change in catalytic activity with supports may be attributed, at least as one of the factors, to the change in the oxidation state of rhodium: larger amount of reduced Rh, better catalytic performance. The order of resistibility against oxidation is in good agreement with that of dispersion after reaction determined by XPS, suggesting a relationship between both resistibility and dispersion. Therefore, the enhancement in the activity shown by grafted catalysts related to bare silica, is mainly due to the capability of grafted supports to keep Rh in a highly reduced and dispersed state. Moreover, the grafted catalysts are also more active than pure titania. As previously indicated, the rutilization of Rh/TiO_2 is observed with increasing temperature, which probably produced a loss in the surface area leading to decreasing the number of active sites compared to Rh on grafted supports, where no rutilization is detected. Therefore, Ti-grafting stabilizes anatase against the rutilization, avoiding the loss in the activity. It has been shown that Ti-grafting gives rise to two different Ti-species: titanium in the Ti–O–Si bonds and, on the other hand, to anatase nanoparticles. As indicated earlier, Ti-grafting also modifies the acidity. Grafted samples are more acid than silica and their acidity is lower compared with pure titania. In addition, new Brönsted acid sites are generated, which are presumably related to the interaction between titania and silica, being higher on the support having a larger number of Ti–O–Si bonds ($13Ti–SiO_2$). It should be noticed that increasing the titanium amount led to enhancing the activity and favouring H_2 selectivity, which corresponds to the largest acidity and/or Ti–O–Si bonds. It is obvious from the above discussion that the improvement in catalytic activity and H_2 selectivity with the increase of TiO_2 content may be attributed to the extent of titania silica interaction (Ti–O–Si bonds) through the generation of new properties which could favour the reduction and/or the dispersion of rhodium.

5. Conclusions

Ti-grafting led to modifications in the surface of the catalysts that affect significantly their catalytic behaviour. The interaction between Ti and SiO_2 through the formation of Ti–O–Si was observed; Moreover, TiO_2 nanoparticles were formed on the silica surface for the highest Ti loading. The parallel accompanying increase in the activity and in H_2 selectivity in the POM seems closely related to the Ti-grafting over silica surface. These positive effects of TiO_2 could arise from its ability to modify redox properties and dispersion of Rh-supported catalysts. These results suggest guidelines for the design of very active and selective Rh-based catalysts in the partial oxidation of methane for producing hydrogen.

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