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Influence of H_2, CO and CO_2 co-feeding on the catalytic activity of Rh/Ti–SiO_2 during the partial oxidation of methane

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ABSTRACT

The influence of the addition of 1, 2 or 5 vol.% of CO, H_2 or CO_2 to the feed during the partial oxidation of methane (POM) was studied over a Rh/Ti–SiO_2 catalyst. The addition of H_2 or CO decreases the conversion and syngas selectivity. This decrease of performance seems to be related to a higher reduction of the catalyst due to the co-feeding of H_2 or CO. The addition of CO_2 also appears unfavourable to the production of hydrogen but increases the CO yield. A combination of the dry reforming and the reverse water–gas shift reactions is suggested to explain the observed modifications in the product yields.

1. Introduction

Due to the increasing demand for hydrogen and clean fuels, the partial oxidation of methane (POM) into syngas is receiving growing attention. Supported Rh catalysts are usually reported as very active and selective catalysts to perform this reaction [1]. Two general mechanistic schemes have been proposed for POM reaction, although no unified point of view has been reached yet, in particular for the reaction pathway over noble metals. Prettre et al. [2] proposed the indirect mechanism involving the total oxidation of a part of CH_4 followed by endothermic reforming of the remaining CH_4 with CO_2 and H_2O to produce syngas. Hickman and Schmidt [3] earlier suggested the direct partial oxidation of CH_4 to CO and H_2. This mechanism has been identified as the main pathway over Ru [4], Rh [5–8] and Pt [9] catalysts. However, the formation of syngas over the same catalysts via the indirect mechanism has been proposed as the main route in [10–14]. For most catalysts, at a mechanistic level, the POM (Eq. (1)) is proposed to proceed as a two-step reaction [1]. The first step involves the total combustion (TOM; Eq. (2)) of some methane by oxygen to give carbon dioxide and water. This is followed by carbon dioxide (or dry reforming, DR; Eq. (3)) and steam reforming (STR; Eq. (4)) of the unreacted methane to obtain synthesis gas. The above reactions are also accompanied by the water gas shift reaction (WGS; Eq. (5)), which affects the final composition of the product gases.

$$\text{POM}: \quad CH_4 + 1/2O_2 \leftrightarrow CO + 2H_2 \quad (\Delta H^{\circ}_{298} = -35\ \text{kJ/mol}) \tag{1}$$

$$\text{TOM}: \quad CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \quad (\Delta H^{\circ}_{298} = -801\ \text{kJ/mol}) \tag{2}$$

$$\text{DR}: \quad CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (\Delta H^{\circ}_{298} = +261\ \text{kJ/mol}) \tag{3}$$

$$\text{STR}: \quad CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (\Delta H^{\circ}_{298} = +206\ \text{kJ/mol}) \tag{4}$$

$$\text{WGS}: \quad CO + H_2O \leftrightarrow CO_2 + H_2 \quad (\Delta H^{\circ}_{298} = -41\ \text{kJ/mol}) \tag{5}$$

It is well recognized that dynamic processes occur on catalysts during catalytic reactions [15]. Under reaction conditions, the catalysts can be modified in many different ways: active sites are created and/or regenerated, oxide-reduction cycles are involved, active new phases are developed, eventually the catalyst is deactivated, etc. The improvement of performances and selectivity and the control of deactivation of catalysts require the knowledge of the effects induced by these dynamic processes on the architecture of the catalyst active sites during the reaction. A promising approach to study these dynamic phenomena, at the surface of oxides at work, consists in the addition of gaseous promoters in the reaction feed [16–19]. The addition of gas co-feeds allows tuning the activity and/or selectivity of the catalyst at work and also providing a new tool to master "*in situ*" the dynamic phenomena occurring at the surface of catalysts. In particular, it appears as a potential means to stabilize the superficial atoms in their most efficient state

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and, coupled with thermodynamic calculations, allow studying dynamic processes involved during reaction. In addition, this method is very attractive as it can be applied directly under operating conditions. On the other hand, the study of the effects of the reaction products as gas promoters in catalytic performances give important information concerning the role of the reaction products on the deactivation of catalysts. In line with previous work [20,21], where this method was applied in the study of POM over supported Ni and Rh catalysts using pure alumina as carrier, the goal of the present contribution is to investigate the influence of the gas co-feeding to the POM on supported Rh catalysts on a different support, namely Ti modified SiO_2. The objective is to study the influence of the nature of support on the gas promoters' effects. The catalytic performance was studied as a function of (i) in the absence of co-feeds, (ii) in the presence of co-feeds (CO, H_2 and CO_2), all of them are POM reaction products, and (iii) varying the concentration of co-feed (1, 2 or 5 vol.%). Experimental results are compared with thermodynamics predictions. The reversible character of the modifications induced by the addition of gas co-feeds is also evaluated. The main physico-chemical properties affecting catalytic performance (dispersion and oxidation state of Rh) were studied by XPS. Finally, the influence of the nature of the support is also discussed (Al_2O_3 vs. Ti–SiO_2), when comparing the results of the present work with those reported before for Rh/Al_2O_3 catalysts [20]. Moreover, the reducing character of CO and H_2 and the oxidant nature of CO_2 could modify the oxidation state of Rh, which is well-known to strongly impinge on catalytic behaviour in POM. On the other hand, a study concerning the reversibility of the changes induced by the co-feeds has been performed. An important question to be answered is whether such modifications are reversible or not. It is out of the scope of this work to discriminate between the two mechanisms proposed in the literature for POM reaction.

2. Experimental

2.1. Preparation of catalyst

A Rh/Ti–SiO_2 catalyst (13 wt.% TiO_2; 0.8 wt.% Rh; Ti–SiO_2 = 98 m^2/g) was synthesized by the wet impregnation method using a $(NH_4)_3RhCl_6{\cdot}3H_2O$ precursor (a detailed description about the preparation and the physico-chemical properties of this catalyst is given in [22]). After impregnation, the catalyst was dried at 110 °C for 16 h and calcined in air at 700 °C for 4 h.

2.2. Catalytic activity

All the tests were carried out at atmospheric pressure in a conventional fixed bed reactor. Two type of tests were performed: (i) *standard test* (in the absence of co-feeds): a 5 vol.% CH_4, 2.5 vol.% O_2 and 92.5 vol.% N_2 gaseous mixture was used, and (ii) *tests in the presence of co-feeds*: were performed by adding 1, 2, or 5 vol.% of CO, H_2 or CO_2 to the feed; in addition, in order to study the transition state of the catalyst due to the introduction of a co-feed, a test alternating the presence (5 vol.% of CO or H_2) or absence of gaseous co-feeds (standard test) was performed (run test). In all cases, the space velocity was maintained constant by balancing with N_2 (total flow = 100 ml/min over 100 mg of catalyst). Prior to the reaction, the catalyst was reduced *in situ* under a pure H_2 flow at 600 °C for 3 h. The catalytic activity was recorded between 400 and 700 °C. The catalyst was cooled down under the reaction conditions. The products and reactants were quantified using a VARIAN gas chromatograph (two thermal conductivity detectors and five columns). The relative error on the measurements of conversions and yields was inferior to 5%. In order to check the accuracy of the obtained data; all tests were doubled; the recorded results were nearly the same in both measurements. The yields and selectivities presented here correspond to the amount of CO, H_2 or CO_2, actually produced. Indeed, they were calculated taking into account the difference between the measured and introduced quantities. The conversion of methane, X (%), is defined as the percentage of methane feed which has reacted. The yields, Y (%), are defined as the percentage of the starting methane converted to a specific product and the selectivities, S (%), as being the ratio of yield over conversion.

2.3. Characterization

XPS analyses were conducted on a SSI X-probe (SSX-100/206) spectrometer from Surface Science Instrument (Fisons) working with a monochromatic Al anode (Kα radiation: 1486.6 eV; 10 kV; 22 mA). Charge neutralization was achieved using an electron flood gun adjusted at 8 eV and placing a nickel grid 3.0 mm above the sample. Pass energy of the analyzer was 50 eV and the spot size was 1000 μm in diameter, corresponding to a full width at half maximum (FWHM) of 1.1 eV for the Au4$f_{7/2}$ band of a gold standard. Binding energies were referenced to the C1s peak (C–C, C–H) set a 284.8 eV. For the quantification of elements, sensitivity factors provided by the manufacturer were used. The samples recovered after reaction tests or H_2 pre-treatment were stored under Ar atmosphere in a desiccator until its use.

3. Results

3.1. Catalytic activity

3.1.1. Catalytic activity in the absence of gas co-feeds

The evolution of the performances in the POM reaction in the absence of co-feeds over a Rh/Ti–SiO_2 with the temperature is plotted in Fig. 1. This figure shows that the conversion of methane increases with the reaction temperature. The yields and selectivities towards the products of the partial oxidation of methane (H_2 and CO) also grow with temperature while the yields and selectivities to the total oxidation products (CO_2 and H_2O, this latter product is not shown in Fig. 1) decrease. The POM is favoured by increasing temperature at the expense of the total oxidation. An important aspect to be noticed is the variation of the H_2/CO ratio with temperature. At lower temperatures ($T < 600$ °C) H_2 yields and selectivities are higher than those of CO, as expected from stoichiometric POM. However, this trend is reversed when temperature increases. In fact, in the high temperatures range (600–700 °C) the CO produced exceeds by far the yields in H_2. Moreover, the increasing CO yield with temperature is followed by

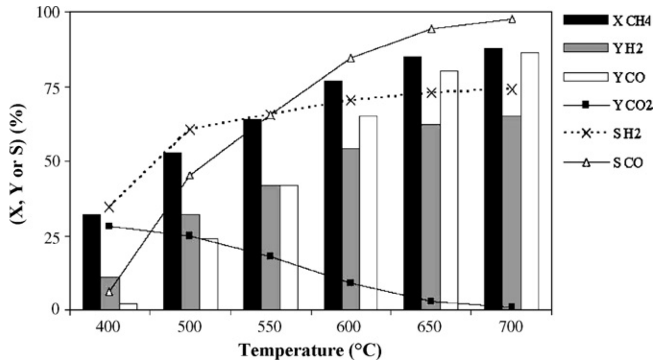

Fig. 1. Catalytic tests. Catalytic performances in POM reaction measured over Rh/Ti–SiO_2 as a function of the temperature.

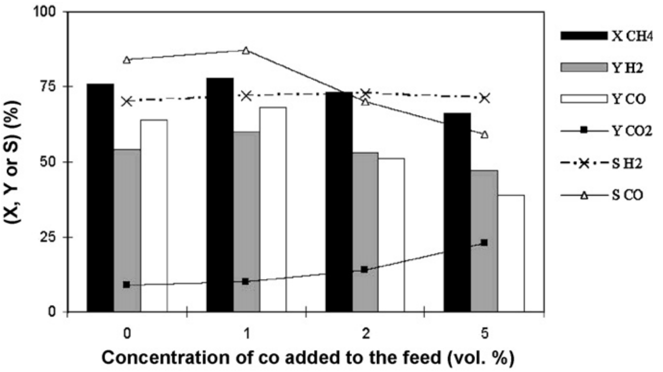

Fig. 2. Catalytic tests in the presence of CO added to the feed. Catalytic performances measured at 600 °C over Rh/Ti–SiO$_2$ catalyst as a function of the CO concentration added to the feed.

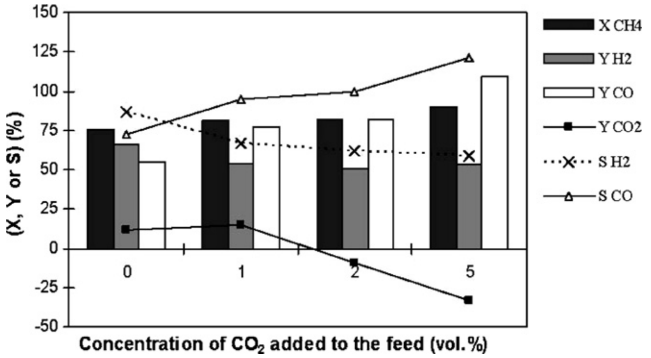

Fig. 4. Catalytic tests in the presence of CO$_2$ added to the feed. Catalytic performances measured at 600 °C over Rh/Ti–SiO$_2$ catalyst as a function of the CO$_2$ concentration added to the feed.

a parallel decreasing in CO$_2$ production. This clearly evidences that other reactions (mainly dry reforming (DR) and reverse water gas shift (RWSG)) take place in the conditions of POM used here.

3.1.2. *Catalytic activity in the presence of gas co-feeds*

The influence of the co-feeds on the catalytic performances depends on the amount of the gas co-feed used. Depending on temperature, a particular discussion could be performed. In this study, the temperature of 600 °C was selected for comparison. Essentially the same conclusions could be obtained comparing the influence of co-feeds at other tested temperatures.

3.1.2.1. Tests performed in the presence of CO as co-feed. The influence of co-feeding CO on the performance of Rh/Ti–SiO$_2$ at 600 °C is shown in Fig. 2. Comparing with results obtained in the absence of CO, the main effects are: (i) A marked decrease in the conversion for higher CO concentrations (5 vol.%); (ii) A gradual decrease in the yields of H$_2$ while increasing amounts of CO are added to the feed. The selectivity to H$_2$ remains essentially unchanged at high amounts of CO co-fed (5 vol.%); (iii) The yields and the selectivities towards CO increase in the presence of 1 vol.% of CO but dramatically decrease in the presence of higher amounts of CO; (iv) CO$_2$ production is significantly enhanced by the addition of high CO concentrations (5 vol.%).

3.1.2.2. Tests performed in the presence of H$_2$ as co-feed. Fig. 3 illustrates the influence of adding various amounts of H$_2$ on the performances of Rh/Ti–SiO$_2$. This figure shows a gradual decrease of the conversion as well as H$_2$ yields and selectivities as the amount of H$_2$ co-fed increases. The selectivity to CO increases first (1 vol.%) and then reaches a plateau (>2 vol.%). The production of CO$_2$ is not appreciably affected by the addition of H$_2$ to the feed.

3.1.2.3. Tests performed in the presence of CO$_2$ as co-feed. The co-feeding of CO$_2$ improves the conversion and the formation of CO (Fig. 4). Nevertheless, it negatively affects the selectivity and yield in H$_2$ that decrease progressively as the amount of CO$_2$ co-fed increases (Fig. 4). On the contrary, the selectivity to CO increases proportionally with increasing amount of CO$_2$ introduced in the feed. An important fact to be noticed is that CO$_2$ yields decrease steadily with increasing amounts of CO$_2$ co-fed, and become negative if more than 1 vol.% of CO$_2$ is added.

3.1.2.4. The three-run test. It is clear from the previous results that the introduction of gaseous co-feeds induces changes affecting catalytic performances. In order to shed some light on this matter, additional tests in the presence or absence of H$_2$ or CO into the feed (5 vol.%) were conducted on Rh/Ti–SiO$_2$ at 600 °C. Fig. 5 shows the activity measurements recorded during the three-run test when a 5 vol.% of H$_2$ is added to the feed. When a 5 vol.% H$_2$ is fed to Rh/Ti–SiO$_2$ (2nd run, Fig. 5), a significant diminution in the conversion and in H$_2$ selectivity is observed; the selectivity to CO markedly increases. Activity measurements recorded during this 2nd run were essentially the same as those previously discussed. When H$_2$ is removed from the feed and the catalyst maintained under standard POM feed (3rd run, Fig. 5), the initial values for conversion, yields and selectivities observed during 1st POM run (Fig. 5) are fully restored, indicating that the effects caused by H$_2$ co-feeding are reversible.

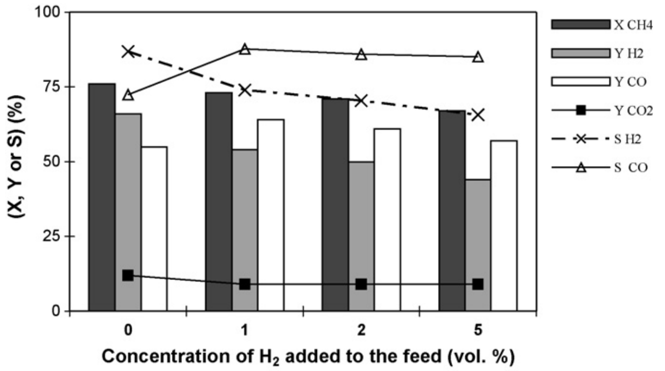

Fig. 3. Catalytic tests in the presence of H$_2$ added to the feed. Catalytic performances measured at 600 °C over Rh/Ti–SiO$_2$ catalyst as a function of the H$_2$ concentration added to the feed.

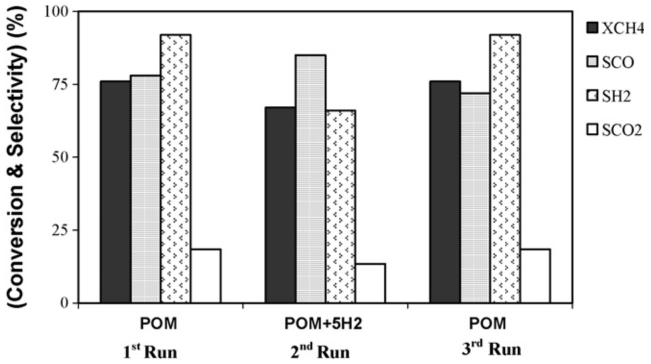

Fig. 5. Catalytic performances measured over Rh/Ti–SiO$_2$ catalyst as a function of the various conditions used at 600 °C (denoted "three-run" test).

Table 1
Summary of XPS data of $Rh/Ti–SiO_2$ catalyst fresh, reduced and after activity tests in absence or presence of co-feeds.

Catalyst	Rh/Ti + Si at. ratio ($\times10^{-4}$)	C/Ti + Si at. ratio	BE Rh $3d_{5/2}$ (eV)	H_2/CO[a] ratio
Fresh	63	0.19	309.1	–
Pre-reduced	33	0.20	307.2	–
After POM	39	0.21	307.4	1.2
After POM + 1% CO	24	0.18	308.2	0.8
After POM + 2% CO	18	0.19	308.1	1.0
After POM + 5% CO	21	0.19	307.8	1.4
After POM + 1% H_2	27	0.16	307.5	0.8
After POM + 2% H_2	26	0.18	307.5	0.8
After POM + 5% H_2	22	0.17	307.3	0.8
After POM + 1% CO_2	25	0.17	308.1	0.7
After POM + 2% CO_2	21	0.16	308.2	0.6
After POM + 5% CO_2	22	0.18	308.5	0.5
After 3-run test (5% H_2)	15	0.15	307.3	0.8
After 3-run test (5% CO)	17	0.17	307.4	1.2

[a] H_2/CO ratio measured at 600 °C over a $Rh/Ti–SiO_2$ catalyst after the activity tests in various conditions (with or without co-feeds).

XPS results corresponding to the catalyst recovered after this test also reflect differences as to the dispersion and oxidation state of rhodium compared to the catalysts after standard POM (without co-feed) (Table 1 and Fig. 6). There is a decrease of the Rh/Ti + Si atomic ratio which reflects a loss of dispersion during the three-run test (Table 1). The catalyst recovered after such a test is reduced in the same extent as that recovered after standard POM and after H_2 as co-feed ($Rh3d_{5/2}$ B.E. = 307.3 eV). Finally, the various conditions employed do not induce any change of the surface C content. Experiments analogous to those described above were conducted but using CO instead of H_2 as co-feed. Results, not presented here for the sake of clarity, showed the same tendency when CO was used as co-feed.

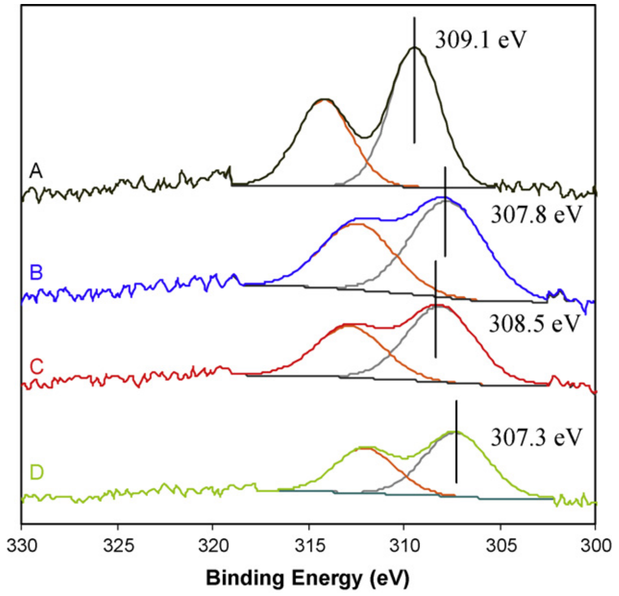

Fig. 6. XPS Rh 3d peaks of (A) fresh $Rh/Ti–SiO_2$, (B) $Rh/Ti–SiO_2$ after test in the presence of 5% of CO, (C) $Rh/Ti–SiO_2$ after test in the presence of 5% CO_2 and (D) $Rh/Ti–SiO_2$ after test in the presence of 5% H_2.

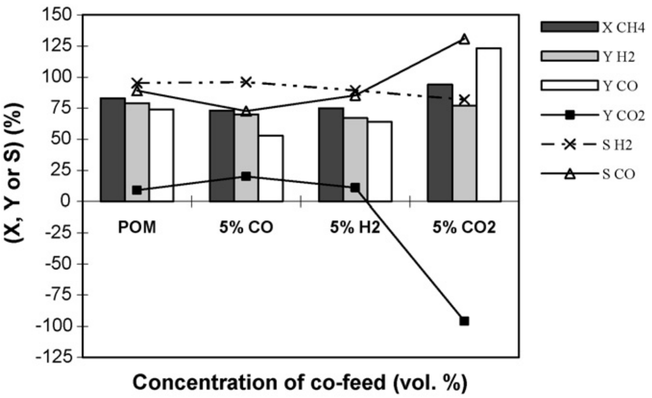

Fig. 7. Thermodynamic equilibrium results in function of the various co-feeds added to the feed in the partial oxidation of methane at 600 °C.

3.1.2.5. Thermodynamic calculations. Fig. 7 gives the thermodynamic equilibrium results calculated for the addition of 5 vol.% of CO, H_2 or CO_2 to the POM feed at 600 °C. Compared to thermodynamic calculations the major effects induced by co-feeding H_2, CO or CO_2 on the catalytic performances of a $Rh/Ti–SiO_2$ catalyst can be summarized as follows:

- The addition of CO leads to a decrease in the conversion and yields in syngas, as thermodynamically expected, but the H_2 yield is experimentally higher. The increase in CO_2 yield is quite smaller related to thermodynamic data. The trend exhibited by the experimental H_2 (decrease) and CO (decrease but weakly) selectivities does not agree with thermodynamics.
- In the presence of H_2, the yields in H_2 and CO are expected to decrease according thermodynamics, but the CO yield slightly increases and the H_2 yield decreases to a larger extent than expected.
- Concerning CO_2 co-feeds, the main difference between experimental and thermodynamic data is found in H_2 yields and selectivities. When CO_2 is introduced into the feed, the selectivities and yields in H_2 are reduced to a larger extent than thermodynamically expected. The addition of CO_2 to the feed leads to negative yields in CO_2, but they occur to a much smaller extent than thermodynamic predictions.

3.2. Characterization results

The various samples were characterized by XPS as fresh, after reducing pre-treatment and after catalytic tests; the results are presented in Table 1. It is observed that in the fresh catalyst Rh is in an oxidized state (~309.1 eV), typical of Rh_2O_3 it is severely reduced after the *in situ* pre-treatment (~307.2 eV), evidencing the presence of metallic rhodium (Rh^0). The presence of carbon was detected over all samples but the surface C content is very stable among the various samples implying that there is no preferential coke deposition on the surface of the catalyst during the tests.

The oxidation state of Rh is also modified by co-feeding of H_2, CO or CO_2 (Table 1 and Fig. 6). Compared to the standard POM test the main effects induced by the presence of gaseous co-feeds are the following: (i) the addition of low amounts of CO (1 or 2 vol.%) to the feed causes a weak reoxidation of Rh (308.2 eV), but the co-feeding of 5 vol.% of CO reduces Rh (307.8 eV) to the same extent as standard POM test. In the presence or absence of CO Rh is partially reduced (Rh^+); (ii) a reduction of Rh as H_2 is added to the feed. It should be noticed that $Rh3d_{5/2}$ photoelectron signal shifts to lower binding energies values (Rh is reduced to a large extent) with increasing H_2 co-fed (307.3 eV for 5 vol.% of H_2); (iii) a reoxidation in the presence of CO_2, which is more noticeable for the test performed adding 5 vol.% of CO_2 (308.5 eV).

There is a sintering of the rhodium phase after reductive pre-treatment, as evidenced by the decrease of the Rh/Ti + Si ratio

(63×10^{-4} vs. 33×10^{-4}). After POM the XPS Rh/Ti + Si atomic ratio slightly increases, which could be due to the fact that some rhodium migrates to the catalyst surface (re-dispersion) during reaction. As shown in Table 1, the addition of co-feeds also induces the sintering of the rhodium phase (compared with standard POM). Sintering is somewhat stronger than after standard POM (Table 1).

4. Discussion

4.1. The dynamics of the reaction

The co-feeding of H_2, CO or CO_2 induces changes in the performances of supported Rh catalysts which are not fully explained by thermodynamics. On the other hand, XPS results for the catalysts recovered after various tests performed adding H_2, CO or CO_2 reveal modifications in the oxidation state of rhodium and/or in the dispersion, compared with the results obtained over the catalysts after standard POM. It is recognized that both oxidation state and dispersion of rhodium affect the activity and the selectivities to syngas in the POM reaction. Thus, one can conclude that the changes observed with co-fed gaseous promoters can be explained by modifications in the solid state of supported Rh catalysts (in particular, changes in the oxidation state of rhodium).

The run test showed that the catalytic modifications induced by the gaseous promoters are reversible. This seems to indicate that the main role of gaseous promoters is to modify the oxidation state and dispersion of rhodium during the reaction. Once the gas promoter is stopped, the oxidation state of Rh goes back to the oxidation state typical of POM, evidencing that the oxidation state of Rh strongly depends on the composition of the reactant mixture. The conversion of methane and yields of products will depend on the oxidation state of Rh, but a change in the oxidation state of Rh implies a change in the kinetics of the reactions involved during POM. These changes in the kinetics could explain the changes in the performances in POM.

One point is important to be underlined. In the reversibility test, changes in the oxidation state were observed, when H_2 or CO were co-fed. At the end of the 3th run, the oxidation state of Rh was the same as in the 1st run (standard test) or after standard POM. However, it seems that the dispersion of Rh was smaller after the 3th run. The reproducibility after one, two- or three-runs was remarkable. This indicates that, probably, the most important parameter influencing the catalytic performance in POM is the oxidation state of Rh (at least in the experimental conditions of the present study). A further decrease in the dispersion seems to have little influence in the catalytic activity or selectivity. This can be understood considering that in the conditions of the present study, the differences in the dispersion of Rh are not too large, and thus, such small changes could weakly affect catalytic performances.

As discussed previously [20,21], these results have implications in the expression of the reaction kinetics to be used in the modelling of the reaction mechanism. At present, the kinetic equation considers the mechanism of the reaction and the number of active sites in an only one-term equation. A two-term kinetic equation could be proposed: one considering the reaction mechanism occurring in each active site and the other considering the number of active sites when such a run-reaction operates. The global equation has to consider all equations which operate during the partial oxidation of methane.

On the other hand, compared to the results obtained over Rh/Al_2O_3 [20], it can be observed that the co-feeding induces similar global effects on the catalytic performances of Rh/γ-$Al_2O_3$and Rh/Ti–SiO_2. However, some differences in the catalytic and physico-chemical properties of both catalysts are also detected, in particular in presence of CO or H_2. The main discrepancies between both samples are the following:

- The co-feeding induces a slight decrease of the dispersion in the case of Rh/Ti–SiO_2 catalyst, instead of a huge increase as in the case of Rh/γ-Al_2O_3.
- After standard POM, Rh/Ti–SiO_2 catalyst is more highly reduced than Rh/γ-Al_2O_3.
- The presence of 5 vol.% of CO causes the decrease of the CO selectivity over both catalysts but such a decrease occurs in a greatly larger extent in the case of Rh/γ-Al_2O_3.
- The addition of 5 vol.% of H_2 into the feed results in a small decrease of the selectivity towards H_2 for Rh/γ-Al_2O_3 whereas it is slightly increased on Rh/Ti–SiO_2.

In previous works [20,21], it was demonstrated that the changes occurring in the presence of co-feeds are influenced, in some extent, by the active phase (Ni or Rh). The present results go further and indicate that the modifications caused by co-feeding depend also on the nature of the support (γ-Al_2O_3 or Ti–SiO_2). Additional experiments are being performed in order to support this explanation.

4.2. The influence of other reactions

The catalysts studied in this work appear to be active in the DR and WGS [23] reactions in the same range of temperature as considered here. Therefore, it is quite reasonable to suggest that a complex scheme of side or parallel reactions takes place in the conditions of POM over supported Rh catalysts. This latter has been reported beforehand for Ni/γ-Al_2O_3 catalysts [20,25,26]; indeed, a pathway involving dry reforming (DR), steam reforming (STR), (reverse) water–gas shift (RWGS) and the total oxidation of methane (TOM) is commonly accepted over based Ni catalysts. The addition of gaseous co-feeds can consequently modify activities, yields, and selectivities of all these reactions in a different way as thermodynamically expected.

As mentioned earlier, the activity data recorded in the absence of gaseous co-feeds (standard POM conditions) showed that at high temperatures (600–700 °C) the yield in CO is considerably higher than that in H_2, which is not expected from stoichiometric POM ($YH_2 > YCO$). Moreover, such an increase in CO yields is followed by a parallel decrease in CO_2 production. These results can be easily understood if one considers the occurrence of other reactions (mainly DR and RWGS) influencing the product distribution, namely H_2, CO and CO_2. It is thus reasonable to admit that the involvement of the other reactions occurring together with POM constitutes a plausible explanation of changes induced by gas promoters. This is consistent with results previously reported in literature [1,24–26].

5. Conclusions

The co-feeding of H_2, CO or CO_2 during POM clearly affects the performance of the catalysts, leading to changes that do not entirely agree with thermodynamic predictions. Gaseous co-feeding also modifies the oxidation state and in a lesser extent the dispersion of rhodium. Our results seem to suggest that the changes in catalytic performances observed here are due mainly to changes in the oxidation state of Rh. Such changes can alter the kinetics of POM and of the other reactions involved (DR, WGS, STR, TOM, etc.), explaining the modifications observed in the presence of gas co-feeds. This is an interesting information that can be useful in the design of reactors (i.e. membrane reactors), aimed at improving activities and/or selectivities in POM.

It has also been proved that the catalytic modifications induced by gas co-feeds are reversible. The initial levels of conversions, yields and selectivities can be restored by taking off the gas dope from the feed. Changes in the oxidation state were also reversible. Nevertheless, it should be pointed out that although the modifications concerning the catalytic performances and oxidation state appear to be reversible, this does not seem to be the case for the dispersion of rhodium that is, in general, decreased by changes in the reaction atmosphere. Our results seem suggest that: either the observed changes in dispersion are not high enough to affect catalytic performances, or the modifications in the oxidation state of Rh affect to a larger extent the catalytic behaviour in POM than the changes in dispersion.

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