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Modulation of selective sites by introduction of N_2O, CO_2 and H_2 as gaseous promoters into the feed during oxidation reactions

O. Demoulin[a], I. Seunier[a], F. Dury[a], M. Navez[a], R. Rachwalik[b], B. Sulikowski[b], S.R. Gonzalez-Carrazan[c], E.M. Gaigneaux[a], P. Ruiz[a,*]

[a] *Unité de catalyse et chimie des matériaux divisés, Université catholique de Louvain, Croix du Sud, 2/17, 1348 Louvain-la-Neuve, Belgium*
[b] *Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków, Poland*
[c] *Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad de Salamanca, Salamanca, Spain*

In celebration of the 65th birthday of Professor Ferruccio Trifirò.

Abstract

Results obtained by adding gaseous promoters (CO_2, N_2O and H_2) into the reaction feed are presented for two different reactions: (i) oxidative dehydrogenation of propane (ODP), and (ii) catalytic combustion of methane (CCM). The ODP is performed on a mixture of $NiMoO_4$ and CeO_2, by adding 3 vol.% CO_2 into the feed, and on a $NiMoO_4$/[*Si,V*]-*MCM-41* mesoporous catalyst, in the presence of 1 or 5 vol.% N_2O in the feed. The CCM is carried out (i) on Pd(2 wt.%)/$Ce_xZr_{1-x}O_2$ and Pd(2 wt.%)/γ-Al_2O_3 catalysts, on pure CeO_2 and on a mixture of Pd(2 wt.%)/γ-Al_2O_3 and CeO_2 powders, by adding 3 vol.% CO_2 into the feed, and (ii) on a Pd(2 wt.%)/γ-Al_2O_3 catalyst, in the presence of various amounts of H_2 in the feed. It is shown, through all these various examples, that the activity and/or the selectivity of catalysts can be improved by tuning, in a very controlled manner, the oxidation state of active sites via the use of these gaseous promoters.

Keywords: Gaseous dopant; CO_2; N_2O; H_2; Oxidative dehydrogenation; Catalytic combustion

1. Introduction

The addition of gaseous promoters in the reaction gas feed is a promising approach to master the selectivity and/or activity of catalysts at work, in particular to stabilize the superficial atoms in their most efficient state. This method seems to be very attractive because it can be applied directly under the currently operating conditions, without introducing any modification in the established process. Eventually, the gaseous promoters can be added in different sections of the reactors depending on the operation conditions in the section, and their amount can be increased, lowered or even stopped without modification, at will. However, a very few fundamental studies, aimed at elucidating the role of these promoters, have been published so far [1–3].

Previously [4–7], we reported the effects brought about by the introduction of CO_2 or N_2O as gaseous additives during the oxidative dehydrogenation of propane (ODP) to propylene using $NiMoO_4$ alone or in mixture with α-Sb_2O_4 as catalysts. With respect to the results obtained in the absence of CO_2, the main consequences of the addition of CO_2 in the gas feed were: (i) an increase in the conversion of propane, (ii) a decrease in the yield and selectivity of propylene, and (iii) an increase of the CO_2 yield. These results indicate unambiguously that CO_2 can modify the nature of the active and selective sites ‘‘during’’ the selective oxidation reactions. This is surprising because thermodynamics disfavors the conversion of CO_2 to CO and O_2. By working with a small amount of O_2 in the reaction feed (0.5 vol.%), it was demonstrated that, in the absence of CO_2, coke is formed and the catalyst rapidly deactivates. However, if CO_2 is added to the feed, coke formation is inhibited and the catalyst does not deactivate [4]. Pure CO_2 succeeds in oxidizing a reduced oxide sample much more

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[*] Corresponding author. Tel.: +32 10 47 3597; fax: +32 10 47 3649.
E-mail address: ruiz@cata.ucl.ac.be (P. Ruiz).

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rapidly and efficiently than pure O_2 does. This allowed us to conclude that CO_2 can act as an (very powerful) oxidant at low temperature. The results are rationalized by considering that, at low temperature, the CO_2 could dissociate on the surface of the catalyst (CO_2 (g) = CO (ads) + (O^*)) and that the formed oxygen species O^*, is able to induce the change of the oxidation state of metal-containing oxides at the reaction temperature. The activity and the selectivity of catalysts might be dependent upon this process. During the catalytic reaction, CO_2 succeeds in maintaining the structure of the catalysts in a rather higher oxidized state, even when a relatively high hydrocarbon to oxygen ratio is applied, thus giving quite a reductive atmosphere [4,6].

It was also previously demonstrated that the addition of 300 ppm N_2O modifies the catalytic performances of the same catalyst in the same reaction by, principally: (i) decreasing the conversion of propane and oxygen, (ii) increasing the yield and the selectivity to propylene, and (iii) decreasing the yield and the selectivity to CO_2 [5]. In the presence of N_2O, catalytic sites work in a more reduced state and, consequently, in a more selective way. We have suggested that N_2O could inhibit the adsorption of O_2, thus limiting the formation of the non-selective oxygen species (from O_2) and/or the oxidation rate of the catalysts. When the amount of N_2O is higher than 300 ppm, another phenomenon probably takes place. Oxygen species coming from N_2O dissociation could also play a role, suggesting that, while being less oxidant than O_2, N_2O is also able to induce the ODP.

The influence of the addition of some CO_2 in the reactants mixture during the catalytic combustion of methane (CCM) was also previously studied [7,8]. The introduction of CO_2 into the feed modified catalytic performances while maintaining a very high selectivity to CO_2 (100%). The results obtained strongly suggested that the effective influence of the presence of CO_2 in the feed actually depends on the kind of support of the palladium active phase [8]. These results were quite surprising since CO_2 is traditionally considered as an inhibiting agent for the CCM reaction [9]. This latter statement is probably right regarding the most commonly used catalyst, i.e. Pd/γ-Al_2O_3, but seems to be no longer valid for the ceria–zirconia based catalysts since these materials showed a higher activity in the presence of CO_2 than without it in the feed [8]. We have suggested that this could be due to the ability of ceria–zirconia to dissociate some CO_2 molecules and to increase the proportion of superficial O atoms bound to Ce [7]. However, these were preliminary results which need to be confirmed further.

In this paper, we will dwell on the above-mentioned concepts and apply them to other catalytic systems. First, in the ODP, we studied the influence of CO_2 using: (i) a physical mixture of $NiMoO_4$ and CeO_2, and (ii) $NiMoO_4$ supported on vanadium-containing MCM-41 mesoporous catalysts. Second, in the catalytic combustion of methane (CCM), we studied the influence of CO_2 using three different formulations of Pd/$Ce_xZr_{1-x}O_2$ in order to verify the previously suggested explanation concerning the activating effect of CO_2 observed on such catalytic systems [7]. Then, Pd/γ-alumina, CeO_2 and a mechanical mixture of both of these materials were tested in the presence of CO_2 to check if some kind of cooperation between phases could be at the origin of the observed effects of CO_2. Finally, the knowledge of phenomena governing the CCM has been extended by discussing results obtained using H_2 as gaseous promoter in the reaction. The choice of this latter compound was based both on its highly exothermal reaction with O_2 as well as on its highly reductive power. Indeed, the oxidation state of the active phase of the Pd supported catalyst is one of the key parameters and, thus, one of the most studied topics in the CCM reaction [10–14]. So, adding H_2 to the feed could allow us to shed more light on this issue and could, perhaps, be an additional tool to master the catalytic sites by modifying their activity and/or selectivity to CO_2.

2. Experimental

2.1. Preparation of catalysts

2.1.1. $NiMoO_4$

Nickel molybdate (58 m^2/g) was prepared by precipitation of a solution containing nickel nitrate and ammonium heptamolybdate following a procedure described elsewhere [4].

2.1.2. CeO_2

Cerium oxide (34 m^2/g) was obtained by a citrate method. Typically, 40 g of $Ce(NO_3)_3$ were dissolved in 150 ml of distilled water and 20.081 g of citric acid were added to the solution. The solution was evaporated in a rotavapor at 313 K. The gel was dried at 343 K during 16 h and calcined under air at 973 K during 3.5 h.

2.1.3. Mechanical mixture of $NiMoO_4$ + CeO_2

The mixture of $NiMoO_4$ and CeO_2 (46 m^2/g) was obtained by mixing mechanically 50 wt.% of each oxide in a suspension of *n*-pentane which was then dried at 383 K overnight. The mixture was not subjected to a calcination step.

2.1.4. [Si,V]-MCM-41

Vanadium-containing MCM-41 sample (976 m^2/g) was prepared using tetraethoxysilane (TEOS), cetyltrimethylammonium chloride (CTACl), vanadyl sulphate, ammonia and water. The material was synthesized at room temperature using the following molar gel composition: 1.0 TEOS:0.033 $VOSO_4$:0.15 CTACl:2.8 NH_3:141.2 H_2O. The mixture was homogenized for 1 h, washed with distilled water and dried at 353 K. The sample was calcined under argon at 823 K for 8 h, followed by calcination in air at the same temperature for a further 8 h. The material prepared in this way had a Si/V molar ratio of 30.

2.1.5. NiMoO4/[Si,V]-MCM-41

Deposition of nickel molybdate on the VMCM-41 was carried out using the citrate method. Thus, aqueous solution of ammonium heptamolybdate and citric acid (80 ml H_2O, 0.8824 g $(NH_4)_6Mo_7O_{24}\cdot 7H_2O$ and 2.800 g citric acid monohydrate) was prepared, followed by an aqueous solution of nickel nitrate (20 ml H_2O and 1.453 g $Ni(NO_3)_2\cdot 6H_2O$). The pH of the aqueous solution of ammonium heptamolybdate and citric acid was kept constant at a value of 6.0 by the addition of ammonium hydroxide. The aqueous solution of nickel nitrate was added drop-wise to the aqueous solution of ammonium heptamolybdate and citric acid. The pH of the solution was still kept constant at a value of 6.0 by the addition of ammonium hydroxide. Then 1 g of [Si,V]-MCM-41 was added to the solution, the mixture was stirred, evaporated after 2 h and finally dried at 393 K overnight. It was calcined at 573 K for 4 h under an oxygen flow (25 ml/min) followed by calcination at 773 K for the next 4 h. Two different catalysts containing 1 and 2 monolayer(s) were prepared following this procedure (124 and 79 m^2/g, respectively).

2.1.6. Pd(2 wt.%)/γ-Al2O3

The catalyst (68 m^2/g) was prepared by the wet impregnation technique as described in [14]. The sample was heated up to 673 K under O_2 (10 K/min), kept 1 h at this temperature under O_2 and, after flushing under N_2 for 30 min, was reduced under H_2(5 vol.%)/N_2 for 3 h. After cooling down under N_2, the sample was calcined for 3 h at 873 K under air in a muffle furnace.

2.1.7. Mechanical mixture of Pd(2 wt.%)/γ-Al2O3 + CeO2

This mixture (49 m^2/g) was prepared following the same method as indicated above (2.1.3.).

2.1.8. Pd(2 wt.%)/Ce1−xZrxO2

Samples were prepared using methods described above (2.1.2. and 2.1.6.). Ceria–zirconia mixed oxides were obtained by the citrates technique detailed for pure CeO_2, but using $ZrO(NO_3)_2\cdot xH_2O$ ($x = 2.2$) along with $Ce(NO_3)_3\cdot 6H_2O$, in appropriate quantities so as to obtain various ceria–zirconia formulations. These precursors were dissolved in deionized water to give 0.1 M solutions. Citric acid monohydrate was added in 10 wt.% excess over the stoichiometric quantity in order to achieve complete complexation of the metal ions. The solution was then evaporated and the gel was dried and calcined, as described in the case of CeO_2. Finally, palladium was deposited by the wet impregnation technique and the samples underwent the above-described gaseous treatment and calcinations processes. Three different kinds of ceria–zirconia based catalysts were obtained with this procedure, namely Pd(2 wt.%)/$Ce_{0.21}Zr_{0.79}O_2$(8 m^2/g), Pd(2 wt.%)/$Ce_{0.50}Zr_{0.50}O_2$(29 m^2/g) and Pd(2 wt.%)/$Ce_{0.82}Zr_{0.18}O_2$(22 m^2/g).

2.2. Catalytic tests

2.2.1. Oxidative dehydrogenation of propane (ODP)

The conditions of the standard test (in the absence of promoter) correspond to the use of a gas mixture containing 10% propane, 10% O_2 and 80% He by volume. Temperature was varied between 673 and 753 K. When a promoter was added, the total flow was balanced with He in order to keep the same space velocity in all experiments.

Three kinds of experiments were performed: (a) adding 3 vol.% CO_2 to the feed using a catalyst formed by a mechanical mixture of $NiMoO_4$ and CeO_2, (b) adding either 1 or 5 vol.% N_2O in the feed using $NiMoO_4$ supported on vanadium-containing MCM-41, and (c) using a gas mixture containing 10 vol.% propane, 5 vol.% N_2O (namely without O_2) and 85 vol.% He using $NiMoO_4$ supported on vanadium-containing MCM-41.

Wide series of catalytic reactions under identical conditions and using $NiMoO_4$ as catalysts were performed in order to study the reproducibility of measurements. Results showed that the data obtained were accurate within about 1% range (in relative) for the conversions of propane and oxygen and within ranges of about 8% (in relative) for the yields of propylene and CO_2. The range of accuracy of the selectivities was about 10% (in relative). Homogeneous gas phase conversion of propane was not observed for any set of catalytic conditions of reaction described. No limitation by intraparticles gas diffusion of reactants was observed [4,5].

2.2.2. Catalytic combustion of methane (CCM)

The conditions of the standard test (in the absence of promoter) corresponded to the use of a 1 vol.% CH_4, 10 vol.% O_2 and 89 vol.% He gaseous mixture. Temperature was varied between 473 and 823 K. In the presence of promoter, the conditions were identical to those of the standard test, maintaining the same space velocity, by varying the He content, as a gas balance. The experiments were carried out as follows: (a) in the presence of CO_2, using (i) Pd(2 wt.%)/$Ce_{0.21}Zr_{0.79}O_2$, Pd(2 wt.%)/$Ce_{0.50}Zr_{0.50}O_2$ and Pd(2 wt.%)/$Ce_{0.82}Zr_{0.18}O_2$, and (ii) Pd(2 wt.%)/γ-Al_2O_3, pure CeO_2 and Pd(2 wt.%)/γ-Al_2O_3 mechanically mixed with CeO_2, (b) in presence of H_2, adding various concentrations of H_2 (0, 1, 2.5, 3.3, 5.0 and 6.2 vol.%) to the feed on Pd(2 wt.%)/γ-Al_2O_3.

2.3. Characterization of catalysts

BET surface areas were measured using a Micromeritics Flowsorb II 2300 instrument by adsorption of nitrogen at 77 K on samples previously degassed at 423 K for 2 h under a flow of 30% N_2/70% He.

XRD was performed on a Siemens D5000 diffractometer using the Kα radiation of Cu ($\lambda = 1.5418$ Å). The 2θ range between 5° and 80° was scanned at a rate of 0.01°/s. Identification of the phases was carried out by using JCPDS database.

XPS analyses were performed on an SSI X-probe (SSX-100/206) spectrometer from Surface Science Instrument (Fisons) working with a monochromatic Al Kα radiation (10 kV, 22 mA). Charge neutralisation was achieved by using an electron flood gun adjusted at 8 eV and placing a nickel grid 3.0 mm above the sample. The analysed area was approximately 1.4 mm^2 and the pass energy was set at 150 eV. In these conditions, the resolution determined by the full width at half maximum (FWHM) of the Au 4f$_{7/2}$ band of a gold standard was around 1.6 eV. For Mo-containing samples, an additional analysis was carried out in order to decompose the Mo 3d signal into different oxidation state species. This analysis was made with a pass energy of 50 eV, corresponding to an FWHM of Au 4f$_{7/2}$ of 1.1 eV. For the measurements, Ni 2p, Mo 3d, Ce 3d, Zr 3d, Al 2p, Pd 3d, O 1s and C 1s bands were recorded, depending on the kind of sample. However, no recording of the Pd signal could be done when some zirconia was present in the sample since this compound obscures palladium peaks, rendering the Pd XPS analysis infeasible [15]. The binding energies were calibrated by fixing the C–(C, H) contribution of the C 1s adventitious carbon at 284.8 eV. For the quantification of the elements, sensitivity factors provided by the manufacturer were used.

In situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) spectra were obtained by using a controlled temperature and environment reflectance cell (Spectra-Tech 0030-102) with ZnSe windows and coupled to a BRUKER EQUINOX 55 infrared spectrometer equipped with an air cooled MIR source with KBr optics and an MCT detector. The sample was placed inside the chamber without packing or dilution. A flow of He was introduced in the DRIFTS cell during 1 h and the spectrum of the original sample collected. Then the cell was fed with the reactants mixture ($CH_4/O_2/He$ = 5/20/75 or $CH_4/O_2/CO_2/He$ = 5/20/10/65 vol.) and the sample was heated up to 773 K under reaction conditions with and without some CO_2 in the feed. The sample was heated in a 50 K stepwise way with a staying time of around 30 min at each temperature (between 473 and 773 K) and spectra were obtained by collecting 200 scans with a resolution of 4 cm^{-1}.

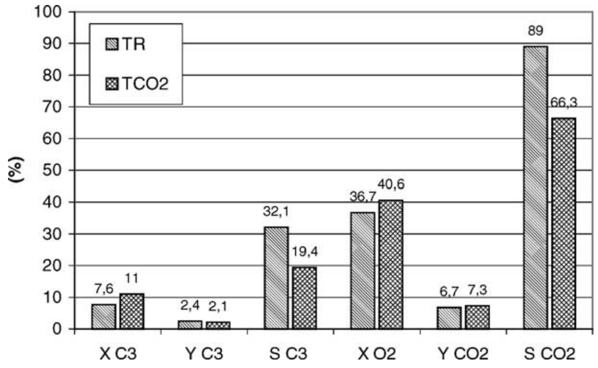

Fig. 1. Comparison of conversion of propane (X_{C_3}), yield (Y_{C_3}) and selectivity (S_{C_3}) to propylene, conversion of oxygen (X_{O_2}) yield (Y_{CO_2}) and selectivity (S_{CO_2}) to CO_2 on $NiMoO_4 + CeO_2$ catalysts at 723 K. TR: test without CO_2, T_{CO_2}: test with 3 vol.% CO_2.

CO chemisorption was performed on a Micromeritics Pulse Chemisorb 2700 apparatus. Samples were pre-treated under H_2 (28 ml/min, 10 K/min) at 673 K for 3 h. After that, a He flow (28 ml/min) was passed during 1 h. After cooling at room temperature, CO pulses (72 μl) were performed.

3. Results and discussion

3.1. Oxidative dehydrogenation of propane (ODP)

3.1.1. CO_2 as gas promoter

3.1.1.1. Physical mixture of $NiMoO_4 + CeO_2$ catalysts. - *Results*: From Fig. 1, it is observed that the addition of 3% CO_2 into the feed leads to: (i) an increase in the propane conversion (+45%), (ii) a decrease in the yield of propylene (−13%), (iii) a decrease in the selectivity to propylene (−40%) and to CO_2 (−25%), and, finally, (iv) an increase in the conversion of oxygen (+11%). Low amounts of a new (probably oxygenated) product were also observed. An attempt to identify this product was made but no conclusive results could be obtained. However, based on its retention time, it was possible to ascertain that it was a light compound. We have attempted to detect the formation of CO but, regarding the rather high sensitivity of our equipment, no indication of CO formation was observed. As CO_2 is produced in the reaction, besides the conversion, the effects observed in the yields of propylene and CO_2, when introducing CO_2 in the feed, are not very pronounced. In addition, the low amounts of propylene formed make even more difficult the evaluation of this compound. Thus, in order to have a more accurate and statistically valid estimation of the results, a multiple realization of the same experiment was carried out under identical conditions. The results presented here show the tendency taking into account the average values obtained in these tests. The objective of this work was principally to detect any change in the catalytic performances due to the co-feeding of CO_2. Considering the degree of accuracy for the measurements of the catalytic performances, these tendencies have to be regarded as significant.

Characterization results of the catalysts studied before and after reaction, either in the presence or absence of CO_2, are similar, except for XPS analyses which show significant differences after test when compared with the fresh catalyst. First, catalysts having worked in the absence of CO_2 show principally: (i) a higher value of the C/Mo atomic ratio (+20%, atomic ratio for fresh catalyst is 2.33), (ii) a decrease of the Ni/Mo atomic ratio (−20%), and (iii) the presence of 4% of total molybdenum as Mo^{5+}. Secondly, for catalysts having worked in presence of CO_2, it can be noticed: (i) a less pronounced higher C/Mo ratio (+12%), (ii) an increase in the Ni/Mo atomic ratio (+16%), and (iii) no presence of reduced molybdenum.

Discussion: These results clearly show that, in the presence of CO_2: (i) catalytic activity is higher, (ii)

Table 1
Catalytic activity results obtained adding 1 and 5% N_2O into the feed during the ODP reaction on 2(monolayers)-$NiMoO_4$/[*Si,V*]-*MCM-41* mesoporous catalysts (50 mg of catalyst) (temperature 753 K)

	Absence of N_2O	Presence of 1% N_2O	Presence of 5% N_2O
Conversion of C_3 (%)	17.0	8.7 (−48%)	9.4 (−45%)
Selectivity in $C_{3=}$ (%)	18.6	44.8 (+141%)	38.2 (+105%)
Yield in $C_{3=}$ (%)	3.2	3.9 (+22%)	3.6 (+13%)

Table 2
XPS analysis

Catalysts	Ni/Si	O/Si	V/Si	Mo/Si	C/Si
Fresh	1.26	8.25	0.06	1.46	2.62
After the test at standard conditions	1.16	8.06	0.04	1.44	2.81
After the test by adding 5 vol.% N_2O in the feed	1.01	7.53	0.04	1.25	2.28
After the test in the presence of N_2O (5 vol.%), propane (10 vol.%) and He (balance) (without O_2)	0.79	7.13	0.04	1.01	17.50

Atomic ratios observed on fresh 2(monolayers)-$NiMoO_4$/[*Si,V*]-*MCM-41* mesoporous catalysts under standard conditions and after test adding 5% N_2O in the feed during the ODP reaction. Temperature 753 K. Results obtained using a gas mixture containing 10% propane, 5% N_2O and 85% He are also shown.

selectivity to propylene decreases, (iii) catalysts work in a fully oxidized state, (iv) the formation of carbonaceous products is inhibited, and (v) some oxygenated product is formed. These results are similar to those previously observed with pure $NiMoO_4$ [4] and with the mixture of $NiMoO_4$ with α-Sb_2O_4 catalysts [6], and seem to confirm the fact that the dissociative adsorption of CO_2 must be taken into account to explain catalytic performance. In the presence of CO_2, the conversion increases by 45% for the mixture with CeO_2, compared to 18% for pure $NiMoO_4$ [4]. This high improvement in the conversion, in the presence of CO_2 in the mixture, might strongly suggest that CO_2 is dissociatively adsorbed on CeO_2, and that the oxygen species coming from dissociation could migrate towards $NiMoO_4$, hence modifying its catalytic activity.

3.1.2. N_2O as gas promoter

3.1.2.1. $NiMoO_4$/[Si,V]-MCM-41 mesoporous catalysts.

- *Results:* From Table 1, it is observed that in presence of 2(monolayers)-$NiMoO_4$/[*Si,V*]-*MCM-41*, the addition of 1 or 5 vol.% N_2O leads to an important decrease in the conversion (−48 and −45%, respectively), a significant increase in the selectivity (+141 and +105%, respectively), and some increase in the yield of propylene (+22 and +13%, respectively). When the amount of N_2O is higher (5 vol.%), a weak increase in the conversion seems to occur (about 4%). This trend could indicate that a minimum in the conversion as a function of the amount of N_2O might be obtained.

XPS results are presented in Table 2. Ni/Si, O/Si, V/Si, Mo/Si and C/Si atomic ratios for fresh catalysts, after standard test, and after test in presence of 5% N_2O, are very similar. We underline the fact that signals of V $2p_{1/2}$ and V $2p_{3/2}$ were masked by the peaks of O 1s and Mo 3s, which made their evaluation very difficult. On the other hand, it was not possible to detect any molybdenum species with an oxidation state lower than 6. This is probably because the amount of molybdenum and nickel in the sample was too low, only two theoretical monolayers. An interesting point is that, in the presence of sole N_2O (i.e. without O_2), a very high amount of carbon was detected after the reaction. This was also observed in the case of pure $NiMoO_4$ catalyst [5].

Discussion: The important improvement in the selectivity due to the addition of N_2O opens wide perspectives for the application of selective mesoporous catalysts. It seems that the principal consequences of the addition of N_2O can be attributed to a decrease of the number of non-selective sites present on the supported mesoporous catalysts. One alternative explanation could be the fact that N_2O inhibits the sites for non-selective propane activation, so leading to a lower conversion, while selectivity increases. The increase of yield may be due to the fact that in a consecutive reaction pattern, the yield to the intermediate species product shows a maximum when increasing reactants conversion, while its selectivity decreases. This explanation could be related to the previous one, namely, the inhibition of non-selective sites in order to avoid the decomposition of the intermediate species into non-selective products. The results obtained when the catalyst contains one monolayer of $NiMoO_4$ were similar, but less significant (when 1 vol.% N_2O is added, conversion decreases from 7.5 to 4.3% and selectivity increases from 34.8 to 41.9%). An interesting result was obtained with 1 (monolayer)-$NiMoO_4$/[*Si,V*]-*MCM-41* catalyst in the presence of 5 vol.% N_2O only (i.e. without O_2). In this case, the conversion of propane was 6.8% and the yield and the selectivity in propylene were 3.2 and 47.5%, respectively. However, the conversion of N_2O was very low (only 0.5%). This result indicates that the propylene formed (3.2%) is not exclusively due to the ODP with N_2O. Propylene is also formed by another mechanism, probably involving lattice oxygen from the catalyst. On the other hand, in the absence of O_2, the catalysts show a very high amount of carbon. This observation indicates that the use of pure N_2O to perform the ODP is not advisable. Molecular oxygen is necessary to oxidize and regenerate the catalysts in the presence of N_2O, otherwise the catalyst deactivates quickly. N_2O reduces the catalysts (molybdenum), explaining the high carbon formation. These results strongly suggest that: (i) a potential role of N_2O in the presence of $NiMoO_4$/[*Si,V*]-*MCM-41* catalyst is to inhibit the non-selective sites, (ii) the formation of propylene by using pure N_2O is very low, and (iii) it is the presence of both O_2 and N_2O (as promoter) that can fully explain the better selectivity of the catalysts in ODP, due to the modulation of their adequate oxidation state during the reaction.

3.2. Catalytic combustion of methane (CCM)

3.2.1. CO_2 as gaseous promoter

3.2.1.1. Pd/$Ce_xZr_{1-x}O_2$ catalysts. Results: The evolution of the conversion of CH_4 as a function of the temperature was followed and compared for a Pd/γ-Al_2O_3 and three types of the Pd/Ce–Zr–O catalysts, namely Pd(2 wt.%)/$Ce_{0.21}Zr_{0.79}O_2$, Pd(2 wt.%)/$Ce_{0.50}Zr_{0.50}O_2$, and Pd(2 wt.%)/$Ce_{0.82}Zr_{0.18}O_2$, both in the presence and the absence of 3 vol.% CO_2. The T_{10}, T_{30} and T_{50} values, which are the temperatures necessary to be reached so as to ensure 10, 30 and 50% of methane conversion, respectively, are listed in Table 3.

As can be seen, the addition of 3 vol.% CO_2 in the gaseous mixture on a Pd/γ-Al_2O_3 catalyst induces a detrimental effect on the activity of such a catalyst (T_{50} = 703 versus 683 K). On the contrary, the addition of 3 vol.% CO_2 in the reactants feed on Pd/$Ce_xZr_{1-x}O_2$ catalysts can lead to a significant increase in the activity of those catalysts (T_{50} = 668 versus 678 K and 708 versus 718 K for Pd(2 wt.%)/$Ce_{0.21}Zr_{0.79}O_2$ and Pd(2 wt.%)/$Ce_{0.50}Zr_{0.50}O_2$, respectively) while keeping a very high selectivity to the desired product (100% in CO_2), thus ensuring an optimal yield of the methane combustion process. Indeed, no CO was detected throughout all the series of the catalytic tests, though the detection limit for this compound was very low indeed (around 40 ppm). The results also indicate that the $Ce_{0.21}Zr_{0.79}O_2$ composition gives rise to the best ceria–zirconia based catalysts whereas the activity of the most highly ceria-loaded based catalyst (Pd(2 wt.%)/$Ce_{0.82}Zr_{0.18}O_2$) was very low, whether in presence of CO_2 or not.

No relevant differences between the catalysts could be identified by applying either BET or XRD techniques to the samples after a test. However, in situ operando DRIFTS experiments seem to evidence the fact that, in the presence of CO_2, a peak centered at 1575 cm^{-1}, assigned to carbonates species [16], can develop on the surface of a Pd/γ-Al_2O_3 catalyst. This is not the case for the Pd/Ce–Zr–O catalyst, working under identical conditions. The XPS characterization results of these various ceria–zirconia based catalysts after test with and without CO_2 in the feed are summarized in Table 4.

First of all, the overall C content in all the samples can be considered as constant, whether the test was run in the presence of CO_2 or not. Moreover, a detailed analysis of the C 1s peak of those samples reveals that the relative proportion of the total amount of carbon which is bound to either C and/or H or to O remains unchanged (result not reported here). Two kinds of O 1s species could be identified: low BE O 1s (below 530.0 eV) and high BE O 1s (above 530.5 eV). The BE value of the low BE species is not influenced by the presence (or not) of some CO_2 in the reactants mixture during the test, while the BE value of the high BE species seems to be more variable. However, enrichment in the proportion of low BE O 1s species can be observed when the catalytic test was run in the presence of CO_2 in the feed, at least for the best catalytic systems, i.e. Pd/$Ce_{0.21}Zr_{0.79}O_2$ and Pd/$Ce_{0.50}Zr_{0.50}O_2$ (68.7 versus 43.0% of total O 1s and 76.1 versus 72.2% of total O 1s, respectively). In particular, this enrichment is more pronounced on the most active catalyst (Pd/$Ce_{0.21}Zr_{0.79}O_2$). Finally, no variation of the Ce/Zr ratio is detected between the tests made with and without CO_2.

Discussion: These catalytic activity results confirm previously reported observations which emphasized the fact that, in CCM, the influence of CO_2 is a function of the type of palladium support [8]. The different behavior towards the presence of CO_2 in the feed between Pd/Ce–Zr–O and Pd/Al_2O_3 catalysts is especially stressed here. Indeed, even if the selectivity remains unchanged (100% in CO_2), the catalytic performance decreases drastically for the Pd/γ-Al_2O_3 catalysts, whereas it is improved for the Pd/Ce–Zr–O catalysts. It is worth noting that: (i) these data confirm previous results concerning the effective role of CO_2 in the CCM reaction [7,8], and (ii) these observations are in

Table 3

T_{10}, T_{30} and T_{50} values for Pd(2 wt.%)/$Ce_{0.21}Zr_{0.79}O_2$, Pd(2 wt.%)/$Ce_{0.50}Zr_{0.50}O_2$, Pd(2 wt.%)/$Ce_{0.82}Zr_{0.18}O_2$ and Pd/γ-Al_2O_3 catalysts, both in absence (−) and in presence (+) of 3% CO_2 in the reactants mixture ($CH_4/O_2/He$ = 1/10/89 vol. and $CH_4/O_2/CO_2/He$ = 1/10/3/86 vol., respectively)

	Pd/$Ce_{0.21}Zr_{0.79}O_2$		Pd/$Ce_{0.50}Zr_{0.50}O_2$		Pd/$Ce_{0.82}Zr_{0.18}O_2$		Pd/γ-Al_2O_3	
	−	+	−	+	−	+	−	+
T_{10} (K)	588	583	613	603	773	783	618	648
T_{30} (K)	643	633	678	668	–	–	658	683
T_{50} (K)	678	668	718	708	–	–	683	703

Table 4
XPS results (binding energy and atomic ratios) of three different ceria–zirconia supported palladium catalysts after test both in absence (−) and in presence (+) of 3% CO_2 in the reactants mixture ($CH_4/O_2/He$ = 1/10/89 vol. and $CH_4/O_2/CO_2/He$ = 1/10/3/86 vol., respectively)

	CO_2 3%	C tot (%)	Low BE O 1s (eV)	High BE O 1s (eV)	Low BE O 1s/O 1s (%)	Low BE O 1s/(Ce + Zr)	Ce/Zr
$Pd/Ce_{0.21}Zr_{0.79}O_2$	−	27.1	529.7	530.8	43.0	1.02	0.085
	+	27.1	529.7	531.6	68.7	1.59	0.086
$Pd/Ce_{0.50}Zr_{0.50}O_2$	−	31.3	529.5	531.4	72.2	1.80	0.286
	+	33.2	529.6	531.6	76.1	1.87	0.289
$Pd/Ce_{0.82}Zr_{0.18}O_2$	−	31.2	529.2	530.6	47.0	1.60	1.546
	+	31.6	529.2	530.5	48.9	1.59	1.596

The O 1s peak could be decomposed into two signals, referred to as low and high BE O 1s peaks, respectively.

contradiction with the commonly accepted inhibiting effect of CO_2 upon the overall reaction process [9].

In order to explain the activating effect of CO_2 noticed on Pd/Ce–Zr–O catalysts during the CCM, we have previously suggested that enrichment in low BE O 1s species, as determined by XPS, could be invoked [7]. Indeed, two kinds of oxygen O 1s species had been identified at the surface of the ceria–zirconia mixed oxide catalysts (low BE O 1s and high BE O 1s). The former would be indicative of O atoms bound to Ce atoms [17] whereas the latter could be assigned to O atoms linked to other elements like C or Zr [7]. After the reaction carried out in the presence of CO_2, the proportion of low BE O 1s species seemed to increase and it was thought to be the consequence of some CO_2 dissociation occurring at the surface of Pd/Ce–Zr–O catalysts. It is worth noting that Ce–Zr–O is well known as an efficient oxygen reservoir. These new results are therefore in very good agreement with those observations, reported earlier for other Ce–Zr–O formulations [7]. Indeed, enrichment in low BE O 1s species is once again observed in the presence of CO_2, at least for the most active catalysts studied here.

This is in line with DRIFTS results. Obviously, the presence of CO_2 in the feed does not induce the development of adsorbed carbonate species on Pd/Ce–Zr–O based catalysts whereas it does on Pd/alumina catalysts. These carbonates species were already observed by Li et al. on a Pd(5 wt.%)/Co_3O_4 catalyst under reaction conditions, but not on a Pd(5 wt.%)/Al_2O_3 catalyst during in situ methane oxidation reaction experiments [18]. They attributed this spectral difference to the lower activity of the latter catalyst at the temperature studied (563 K), since carbonates were thought to be intermediate for producing CO_2. Our results show that these carbonates species can develop on Pd/Al_2O_3, too (at 573 K), but not on Pd/Ce–Zr–O catalysts, in the presence of some CO_2 in the reactants feed. These results are in accordance with the hypothesis of the ability of Ce–Zr–O mixed oxides to activate CO_2, preventing the adsorption of carbonates. Wang et al. came to similar conclusions when studying the influence of CO_2 on CaO–CeO_2 catalysts, even if their study was carried out at much higher temperature (1123 K) [19].

Another key point towards better understanding the effective influence of CO_2 is the fact that there is no difference from the surface C content and/or the C–(C,H)/C ratio viewpoints. This strongly suggests that an influence of the presence of coke at the surface of the catalyst can be ruled out in order to explain the role of CO_2 in the reaction. Moreover, there is no variation of the Ce/Zr ratio between the tests made with and without CO_2 in the flux, indicating that no migration of ceria and/or zirconia can be invoked in order to explain the activating effect of CO_2 on Pd/$Ce_{1-x}Zr_xO_2$ catalysts. This also means that the variations observed in surface in terms of low and high BE O 1s species are not related to modifications of the ratio of the superficial atoms.

Based on both the catalytic tests and the characterization results, it could be suggested that the activating effect of CO_2 observed on Pd/$Ce_{1-x}Zr_xO_2$ catalysts would be the consequence of the ability of ceria–zirconia to dissociate some CO_2 in order to maintain ceria in a highly oxidized state by incorporating O^* species coming from dissociation of CO_2. Then, migration of some O species coming from the ceria–zirconia material would enhance the oxidation state of the palladium, improving the catalytic activity. Another potential pathway involves the direct oxidation of CH_4 molecules by these highly reactive O^* species, produced by the dissociation of CO_2, increasing the overall yield of the CCM.

According to these hypotheses, it is obvious that the ceria compound plays the main role from the effective influence of CO_2 standpoint.

3.2.1.2. Other catalytic systems. Results: Catalytic tests were performed using: (i) Pd(2 wt.%)/Al_2O_3, (ii) pure CeO_2 material, and (iii) a mechanical mixture of Pd(2 wt.%)/Al_2O_3 and CeO_2. The corresponding results are presented in Fig. 2. First, it is obvious that the intrinsic activity of CeO_2 can be considered as being marginal. Second, it is shown that the simple physical contact with CeO_2 allows an increase in the catalytic activity of the Pd(2 wt.%)/Al_2O_3 catalyst (T_{50} = 668 versus 683 K). Moreover, almost no inhibition is observed in this case in presence of CO_2 (T_{50} = 673 versus 668 K).

No significant variation of the BET surface area could be identified on any of these three samples, after test with or without CO_2 in the feed: variations were comprised within

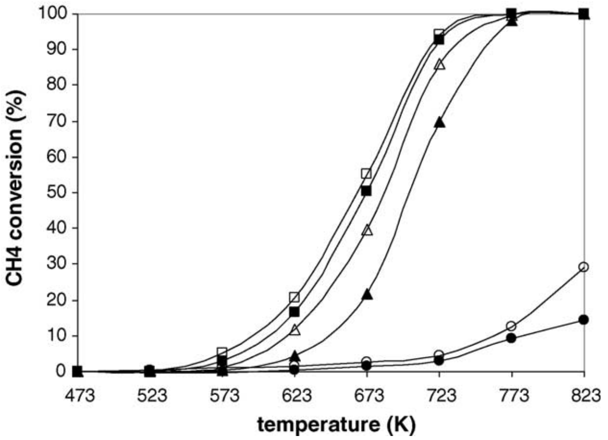

Fig. 2. CH_4 conversion as a function of the temperature on various catalytic systems both with (solid symbols) and without (open symbols) the presence of 3% CO_2 in the feed (CH_4 1 vol.%, O_2 10 vol.%, He balance). Materials are: Pd(2 wt.%)/γ-Al_2O_3(▲,△), CeO_2 (●,○) and a mechanical mixture (50/50 wt.) of Pd(2 wt.%)/γ-Al_2O_3 and CeO_2 (■,□).

the error margin of the apparatus (10%). The XRD results show that the diffraction patterns of the mechanical mixture before as well as after reaction with or without CO_2 are simply the superposition of the structural properties of the two partners. No difference could be detected by XPS concerning the surface state of both Pd/γ-Al_2O_3 and pure CeO_2 after a test with and without CO_2 in the feed. Concerning the mixtures of these components, no reliable data could be obtained since those samples, obtained by slight mixing of both components by means of a spatula, were not homogeneous at all.

Discussion: XRD results clearly indicate that there is no formation of hybrid phases like $CeAlO_3$, for instance, during the reaction process. Thus, the simple physical contact of the Pd/γ-alumina catalysts with CeO_2 allows an increase in its catalytic activity. This result is in good agreement with the hypothesis that some O^* species, formed on CeO_2, might migrate towards the Pd/alumina catalyst, improving its activity. The intrinsic activity of the CeO_2 can be considered as marginal, which implies that the apparent activity of the mechanical mixture reflects a real cooperation between phases (synergistic effect), and is not the simple sum of the intrinsic activities exhibited by each phase. The total amount of catalyst was kept constant in every experiment. The fact that the mechanical mixture is not inhibited by the presence of CO_2 lead us to suggest the hypothesis that CeO_2 is responsible for the increase in the catalytic activity due to the formation and migration of O^* species which could be formed from CO_2. Two arguments seem to support this hypothesis: the similar results observed with mixtures with CeO_2 in ODP, as discussed above, and the increase in the low BE O 1s species, characteristic of oxygen bound to cerium atoms, observed in Pd/Ce–Zr–O catalysts after working under CO_2, both in this work and in a previous paper [7]. This strongly suggests that Ce atoms could be responsible for the activation of CO_2 in the CeO_2 mixtures.

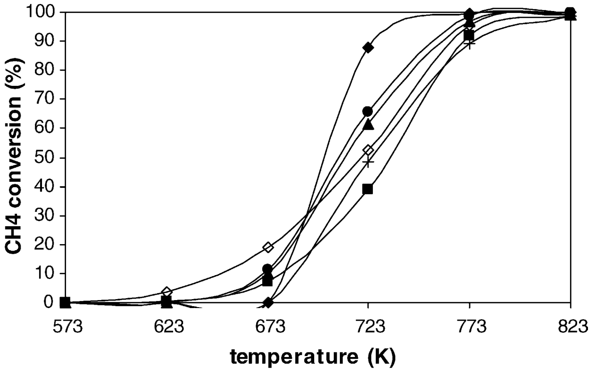

Fig. 3. CH_4 conversion as a function of temperature on a Pd(2 wt.%)/γ-Al_2O_3 catalyst with various H_2 concentrations in the reactants feed (CH_4 1 vol.%, O_2 10 vol.%, He balance): 0% H_2 (◇), 1.0% (■), 2.5% (▲), 3.3% (●), 5.0% (◆) and 6.2% (+).

3.2.2. H_2 as gaseous promoter

3.2.2.1. Results. Fig. 3 shows that the addition of 1% H_2 into the feed induces a detrimental effect on the activity of Pd(2 wt.%)/γ-Al_2O_3 catalysts. Increasing the hydrogen concentration up to 5% leads to a similar effect at low temperature (<673 K), but to a significant gain of activity at higher temperature (>700 K). Further increasing the H_2 concentration up to 6.2% leads to a loss of catalytic activity at all temperatures studied.

The results of physico-chemical characterization of these various samples can be found in Table 5. They indicate that no variation of the BET surface area was observed, under all tested conditions. The dispersion of palladium decreases after test (from 16.3 to 11.3%) and this sintering effect is reinforced when the test is made while adding H_2 in the feed (between 4.5 and 7.4%). However, the importance of the sintering effect of H_2 is independent of its partial pressure; indeed, the dispersion values can be considered as identical along the whole concentration range (1.0–6.2 vol.% H_2) under study. The Pd/Al ratio, as determined by XPS, shows the same trend: this ratio decreases after test, is more pronounced in presence of H_2 but shows the same extent, whatever the H_2 partial pressure may be. Finally, the binding energy (BE) values of the Pd $3d_{5/2}$ peak indicate that, after a test, the palladium is in a highly oxidized state (PdO). This oxidized surface state is observed up to 3.3 vol.% H_2 (336.1 eV); above this hydrogen concentration, the surface metallic palladium is detected at 5.0 and 6.2 vol.% (335.3 and 335.0 eV, respectively). The assignment of BE values observed to the overall surface oxidation state of palladium is based on literature data [11,15,20].

3.2.2.2. Discussion. The principal effect of hydrogen is to inhibit or improve catalytic performances while maintaining the high selectivity of the catalysts. As far as the physico-chemical properties of these various samples are concerned, Table 5 gives information in order to explain the influence of the presence of some hydrogen upon the catalytic activity. First of all, it is clearly shown that a variation of the BET

Table 5
Physico-chemical properties determined by BET, CO-chemisorption and XPS techniques of Pd(2 wt.%)/γ-Al_2O_3 as fresh and after test with 0.0, 1.0, 2.5, 3.3, 5.0 and 6.2 vol.% H_2[a]

H_2 (vol.%)	BET S.A. (m^2/g)	Pd dispersion (%)	Pd/Al ($\times 10^{-4}$)	BE Pd $3d_{5/2}$ (eV)
–	68	16.3	124	336.2
0	67	11.3	115	336.5
1.0	66	7.4	80	336.5
2.5	72	4.6	72	336.4
3.3	69	7.4	85	336.1
5.0	64	7.0	76	335.3
6.2	64	4.5	79	335.0

[a] Fresh catalyst after test.

surface area of the catalyst during the reaction can be definitively ruled out, whether in presence of hydrogen or not. A second point that deserves attention is a very nice correlation obtained between dispersion of palladium, as measured by CO-chemisorption, and surface Pd/Al ratio, as determined by XPS. These two features follow exactly the same trend: they both indicate that the palladium particles sinter during the reaction and that the extent of this surface migration is reinforced by the presence of some hydrogen in the gaseous feed, independently of the H_2 partial pressure, at least at the concentration range investigated.

The origin of the sintering of the palladium particles could be the more reductive atmosphere obtained when adding H_2. Indeed, reductive media favor the appearance of metallic palladium and their rapid coalescence into larger particles, whereas oxidant atmospheres cause the PdO particles to spread onto the alumina support [21,22]. This explanation is well supported by the XPS and Pd dispersion measurements reported in Table 5. Sintering could result also from the highly exothermal combustion reaction of H_2, which probably induces local ‘‘hot regions’’ on the catalysts surface. Indeed, it is well known that the temperature is a key parameter controlling the dispersion of palladium [23]. More precisely, sintering of palladium particles is favored at high temperature. On the other hand, heat produced by the combustion of H_2, has to be evacuated as soon as it is produced. Thus, we cannot exclude that heat transfer also plays a role in the whole set of our data.

Surface dynamic processes are another aspect to be considered in order to explain the role of H_2 in CCM on Pd/γ-Al_2O_3 catalysts. Previously, we have demonstrated, using in situ Raman spectroscopy studies, that on the Pd(2 wt.%)/γ-Al_2O_3 catalysts, palladium is in a fully oxidized form, while the catalyst is under working conditions [14]. This is the more selective and active state of palladium during reaction. More precisely, a layer of a very reactive oxygen species would develop on the surface of the palladium particles, both under pure O_2 atmosphere or under working conditions. If the amount of these species decreases, activity decreases also. Even if the bulk is probably, at least partially, reduced in the presence of hydrogen, the XPS analysis showed that the surface of the palladium is in a full oxidation state, even under quite reductive conditions (up to 3.3 vol.% H_2), thus confirming Raman studies. This implies that, when the oxygen layer is deficient in the reactive oxygen species (due to their consumption by hydrogen), a diffusion process might be established from the bulk of the PdO towards its surface, in order to re-establish this fully oxidized layer.

The highly exothermal reaction between H_2 and O_2 occurs at temperatures as low as 373 K (or even less) on the Pd-based catalysts. Moreover, the light-off temperature of CH_4 is determined by the temperature of the catalyst, which is, in turn, influenced by the heat released by the H_2 oxidation [24]. Accordingly, different situations may be considered: (1) without H_2, the palladium particles are covered with the reactive oxygen species, which ensures a very good activity to the catalyst, (2) the addition of 1 vol.% H_2 slightly reduces the outermost layer of the PdO particles, hence decreasing their activity for CH_4 oxidation. The amount of heat released by such a reaction is too low to balance the detrimental effect of the flush of the oxygen species from the surface of the PdO particles, hence the overall activity of the catalyst is significantly decreased, (3) when more H_2 (up to 5 vol.%) is added to the gaseous feed, the thermal effect resulting from the highly exothermal combustion of hydrogen at the surface of the catalyst is so high that it overcomes the inhibiting effect due to the consumption by H_2 of the O species from the oxygen layer. Simultaneously, some lattice oxygen species are able to migrate through the palladium particle in order to supply the surface with reactive species and the catalyst remains very active, (4) when the amount of H_2 added to the gaseous flow is too high (>5 vol.%), the reduction of the outermost layer is so pronounced that the CH_4 molecules can no longer be oxidized in the optimal conditions and/or the migration rate of the lattice oxygen species towards the surface is too slow to maintain a sufficient amount of active oxygen species on the surface of palladium particles. As a result, an overall deactivation of the catalyst is therefore observed.

Activation energies values seem to support the fact that the mechanism of combustion depends on the amount of hydrogen introduced. In the absence of hydrogen, activation energy is about 10 kcal/mol but in presence of 3.3 vol.% of hydrogen, it increases about twice. When the H_2 partial pressure is higher (5 vol.%), the activation energy increases by a factor of 5. For 6.2 vol.% of hydrogen, values of about

10 kcal/mol are again observed. These values are in line with E_A values reported for methane oxidation on PdO (16–18 kcal/mol) and Pd (40–45 kcal/mol) [12].

Two major implications arise from these results: first, the addition of hydrogen induces changes from the activation energy point of view and, thus, modifies the reaction mechanism of the CCM. Second, the apparent change of E_A is probably due to the combustion of H_2 and not only to the fact that the oxidation state of the palladium has changed from PdO to metallic palladium; this further confirms the fact that the effect of H_2 addition cannot be explained by a reduction of the palladium only.

4. Outlook

The present results confirm the previous ones obtained by using N_2O and CO_2 as gaseous promoters and extend the role of promoter to H_2. We note that important immediate consequences arise from these results:

1. CO_2 and N_2O play an important role in reactions in the presence of oxygen in ODP and CCM. CO_2 promotes oxidation whereas N_2O promotes reduction of catalytic sites during the ODP reaction. Both effects have implication in the selectivity of the catalysts.
2. The injection of controlled amounts of H_2 into the feed can dramatically improve the efficiency in the combustion process. Catalysts with higher performances and still very high selectivity can be obtained in this way.
3. In order to improve the selectivity, it is necessary to tune, in a very controlled manner, the oxidation state of active sites during reaction. There is an optimum of the oxidation state that ensures the maximum of selectivity. This optimum could be adjusted by tuning the amount of gas dopant individually or by performing the simultaneous injection of N_2O and CO_2 "during the reaction". Addition of gas promoters can be directly applied in existing units without any modification of the process.
4. In the forthcoming years, as the hydrogen production will undoubtedly grow, it could be envisaged to add hydrogen to the natural gas which will be distributed in cities (hydrogen-assisted combustion). Up to now, little information has been published regarding the consequences of the addition of hydrogen to the feed on the catalytic performances of catalysts. To summarize, we clearly show in this work, that dramatic changes must be expected in the performance of catalysts used for the combustion of methane in this case.

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