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Modification of active catalytic sites with N_2O and CO_2 as gas promoters during oxidation reactions

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Abstract

The influence of adding 300 ppm of N_2O in the feed during the oxidative dehydrogenation of propane and 3% of CO_2 during the oxidation of methane was studied using a mixture of $NiMoO_4$ and α-Sb_2O_4, and a palladium supported on a mixed Zr-Ce-O oxide catalyst, respectively. In both cases, the selective sites are modified by the presence of the gas dopes. With N_2O, the selectivity to propylene increases, while the conversion of both propane and oxygen and the yield in CO_2 decreases. N_2O promotes the reduction of molybdenum. CO_2 promotes total oxidation of methane. The dissociation of CO_2 seems to be responsible for this promotion. The adjustment of the concentration of N_2O and CO_2 thus clearly appears as a promising tool to improve the selectivity of partial oxidation products and the energetic efficiency in combustion.

Keywords: Oxidation reaction; Gas dopes; Dynamic processes in catalysis; CO_2; N_2O

1. Introduction

Dynamic aspects have to be taken into account in the design of processes, in the modelling of the kinetics and in the design of catalysts [1]. The catalytic sites change in number under the conditions of reaction. Selectivity is correlated with the oxidation state of sites during the catalytic reaction. It is very difficult to maintain, in a controlled manner, the surface in a desired oxidation state without modifying the operating conditions (ratio of the partial pressures of oxygen and hydrocarbon in the gas feed, temperature, catalysts formulations, etc.). A new and promising approach to master the dynamic phenomena at the surface of oxides at work consists in the addition of gaseous dopes in the reaction gas feed. The efficiency of the reactor operation could be improved by injecting adequate amounts of dopes either in the feed or in different sections along the catalyst bed. This method is very attractive because it can be directly applied under presently operating reactors without any modification in the process. However, fundamental studies published in order to explain the role of these promoters in oxidation reactions are scarce. A more detailed experimental approach is thus required in order to understand their exact role during the catalytic reactions. In previous papers, investigating the oxidative dehydrogenation of propane on $NiMoO_4$ catalysts in the presence of CO_2 and N_2O used as dopes, we have shown that CO_2 maintains Mo in a higher oxidation state [2,3]. On the contrary, N_2O inhibits such oxidation, promoting the reduction to Mo^{5+}. CO_2 increases conversion and, thus, favours non selectivity; on the contrary, N_2O decreases conversion and increases selectivity. In both cases, the consumption of oxygen decreases. Contrarily to what is traditionally believed, CO_2 is not inert in the oxidation reaction. Oxygen species produced by its dissociation can modify the oxidation state of the atoms on the surface of the catalysts and can directly participate in the oxidation of the hydrocarbon [2–4].

In this paper, the scope of previous results is extended: (i) study of the role of N_2O in the oxidative dehydrogenation of propane in the presence of a different catalyst, namely a complex biphasic catalyst ($NiMoO_4$ mechanically mixed with α-Sb_2O_4) and (ii) investigation of the influence of CO_2 in the total combustion of methane. The first system has been considered because it was previously demonstrated that α-Sb_2O_4 controls the number of selective sites (probably via spillover oxygen) of active oxide phases during the oxidation reaction [1]. The second system is studied because, in catalytic combustion reactions, a high amount of CO_2 is

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produced during the reaction and it has been thus suggested that CO_2 would act as an inhibitor of the reaction [5]. Catalysts were characterised by BET, XRD and XPS.

2. Experimental

2.1. Preparation of catalysts

Nickel molybdate was prepared by precipitation of a solution containing nickel nitrate and ammonium heptamolybdate following a procedure described elsewhere [2,3]. Two different batches (Batch A and B) were used. α-Sb_2O_4 was obtained by calcination of Sb_2O_3 under static air at 773 K overnight. The mixture of $NiMoO_4$ and α-Sb_2O_4 was obtained mixing mechanically 50 wt.% of each oxide in a suspension of *n*-pentane and then dried at 383 K overnight. No calcination was performed with the mixture.

The ceria-zirconia mixed oxides supports were synthesised by the citrate method, which is fully detailed in [6]. Compounds such as $Ce_{0.37}Zr_{0.63}O_2$, $Ce_{0.70}Zr_{0.30}O_2$ and $Ce_{0.91}Zr_{0.09}O_2$ were prepared in this way. These supports were then impregnated with a palladium containing solution ($Pd(NH_3)_4Cl_2 \cdot H_2O$) by the wetness incipient method [7].

2.2. Catalytic test

2.2.1. Test in the presence and absence of N_2O

Oxidative dehydrogenation of propane (ODP) was performed in a conventional pyrex fixed-bed micro-reactor ($i.d. = 8$ mm) operated at atmospheric pressure with catalyst powder (particles diameter between 200 and 315 μm, 250, 500 or 1000 mg). Both the concentrations of O_2 and propane in the feed were 10 vol.%. Helium was the carrier gas. The total flow rate was set at 30 ml/min. Catalytic activity was measured in the absence and in the presence of 300 ppm of N_2O introduced as gas dope in the feed. The flow of He was balanced so as to ensure that the total gas flow remained unchanged. Temperature was 723 K. Analysis of reactants and products was performed by on-line gas chromatography [3]. The measured performances were accurate within ranges of about 1% (in relative) for the conversions of propane and oxygen and within ranges of about 8% (in relative) for the yields in propylene and CO_2. The range of accuracy on the selectivity was thus about 10% (in relative).

2.2.2. Test in the presence and absence of CO_2

Combustion of methane was performed in a conventional fixed-bed micro-reactor (stainless steel: $i.d. = 8$ mm) operated at atmospheric pressure, into which the catalyst (particles diameter between 100 and 315 μm, 320 mg) was introduced. The total flow rate of the reactants mixture was 100 ml/min and helium was used as carrier gas. Two kinds of tests were performed: (1) using 1 ml/min of CH_4, 10 ml/min of O_2, balanced with He (89 ml/min) and (2) test in the presence of 3% of CO_2 in the gaseous reactants feed with 1 ml/min of CH_4, 10 ml/min of O_2 and 3 ml/min of CO_2, balanced with He (86 ml/min). The reaction was run between 473 and 723 K. The analysis of reactants and products was performed by on-line gas chromatography. The measured performances were accurate within a range of about 1% (in relative) for the conversions of methane and oxygen and within a range of about 4% (in relative) for the yields in CO_2.

3. Results

3.1. Catalytic performances

3.1.1. Addition of N_2O in the feed

Pure α-Sb_2O_4 is completely inert. In both tests, the amount of $NiMoO_4$ is the same. Compared to the results observed using pure $NiMoO_4$, it is observed that the addition of α-Sb_2O_4 induces an important modification in the catalytic performances of $NiMoO_4$ (Table 1): (i) a significant decrease in the conversion of propane (−46%), (ii) a decrease in the yield in propylene (−21%), (iii) a strong increase in the selectivity of propylene (+45%), (iv) a significant decrease in the conversion of oxygen (−41%), (v) an important decrease in the yield of CO_2 (−60%) and in the selectivity in CO_2 (−27%). Clearly, α-Sb_2O_4 inhibits non-selective sites, increasing the selectivity.

Taking into account the precision in the measurements, introduction of N_2O in the feed produces significant changes. When compared with the mixture of $NiMoO_4 + \alpha$-Sb_2O_4 tested in the absence of dope, addition of 300 ppm N_2O in the feed induces (Table 2): (i) a weak decrease in the conversion of propane (−13%), (ii) a decrease in the yield of CO_2 (−22%) and (iii) a decrease in the conversion of oxygen (−21%). The yield (−3.2%) and the selectivity (+8%) in propylene and the selectivity in CO_2 (−9%) remain unchanged. For pure $NiMoO_4$, addition of 300 ppm

Table 1
Catalytic activity results

Test	Catalysts	N_2O (%)	$XC3$ (%)	$YC3^=$ (%)	$SC3^=$ (%)	XO_2 (%)	YCO_2 (%)	SCO_2 (%)
1	$NiMoO_4$ (250 mg)	0	12.8	3.8	29.7	45.4	6.8	52.9
2	$NiMoO_4 + \alpha$-Sb_2O_4 (500 mg)	0	6.9 (−46.0)	3.0 (−21)	43.0 (+45)	27.0 (−41)	2.7 (−60)	38.4 (−27)

ODP on pure $NiMoO_4$ (Batch A) and on $NiMoO_4 + \alpha$-Sb_2O_4 mixture in the absence of N_2O. Temperature 723 K. In all cases propane 10%, oxygen 10% and balance helium. X = conversion, Y = yield. S = selectivity. In parenthesis, changes in comparison with tests without α-Sb_2O_4.

Table 2
Catalytic activity results

Test	Catalysts	N_2O	$XC3$ (%)	$YC3^=$ (%)	$SC3^=$ (%)	XO_2 (%)	YCO_2 (%)	SCO_2 (%)
3	$NiMoO_4$ + α-Sb_2O_4 (1000 mg)	0%	9.3	3.2	34.6	24.9	2.3	24.2
4	$NiMoO_4$ + α-Sb_2O_4 mixture (1000 mg)	300 ppm	8.1 (−13)	3.1 (−3.2)	37.5 (+8)	19.7 (−21)	1.8 (−22)	22.0 (−9)
5	$NiMoO_4$ (250 mg)	0%	14.6	2.7	18.3	38.7	3.4	23.2
6	$NiMoO_4$ (250 mg)	300 ppm	12.4 (−15)	3.0 (+11)	24.2 (+32)	31.5 (−19)	2.7 (−21)	21.4 (−8)

ODP on pure $NiMoO_4$ and on $NiMoO_4$ + α-Sb_2O_4 mixture in the absence and in the presence of 300 ppm of N_2O. $NiMoO_4$ is from Batch B. Temperature 723 K. In all cases propane 10%, oxygen 10% and balance helium. X = conversion, Y = yield. S = selectivity. In parenthesis, changes when comparing tests with and without α-Sb_2O_4 and in the presence and absence of N_2O. Numbers in parenthesis correspond to the difference of performances compared to the previous line (test).

N_2O leads to (Table 2): (i) a decrease in the conversion of propane (−15%), (ii) an increase in the selectivity to propylene (+32%), (iii) a decrease in both the conversion of oxygen (−19%) and the yield of CO_2 (−21%).

A lack in the carbon balance was observed. The sum of percentages of selectivity to propylene and CO_2 is in general about 80%. However, in some cases, values as low as 50% were observed. The values of selectivity in propylene are in the average of values observed in the literature for the ODP on oxide catalysts with this degree of conversion. A lack in the oxygen balance was also observed. Both results suggest that some propane is probably converted into an oxygenated product. No coke formation was observed. The high consumption of oxygen could confirm this fact. We have not observed CO formation during analysis. In fact, CO is easily oxidised to CO_2 on $NiMoO_4$ catalysts. A small peak which was identified as acrolein was observed, both in the absence and in the presence of N_2O. However the area of this peak was not reproducible enough and very difficult to quantify. Experiments have been performed under low conversion of propane, making the analysis of products more difficult. Other possibilities are the formation of an alcohol, an acid, an aldehyde, etc. As the main aim of our investigation was to study changes in conversion, yield and selectivity of the products due to the introduction of N_2O during the catalytic reaction, we have not insisted further in their identification.

3.1.2. Addition of CO_2 in the feed

The addition of 3% of CO_2 into the gaseous feed leads to an increase of the catalytic activity of the various catalysts tested. Indeed, as shown in Fig. 1, the methane conversion

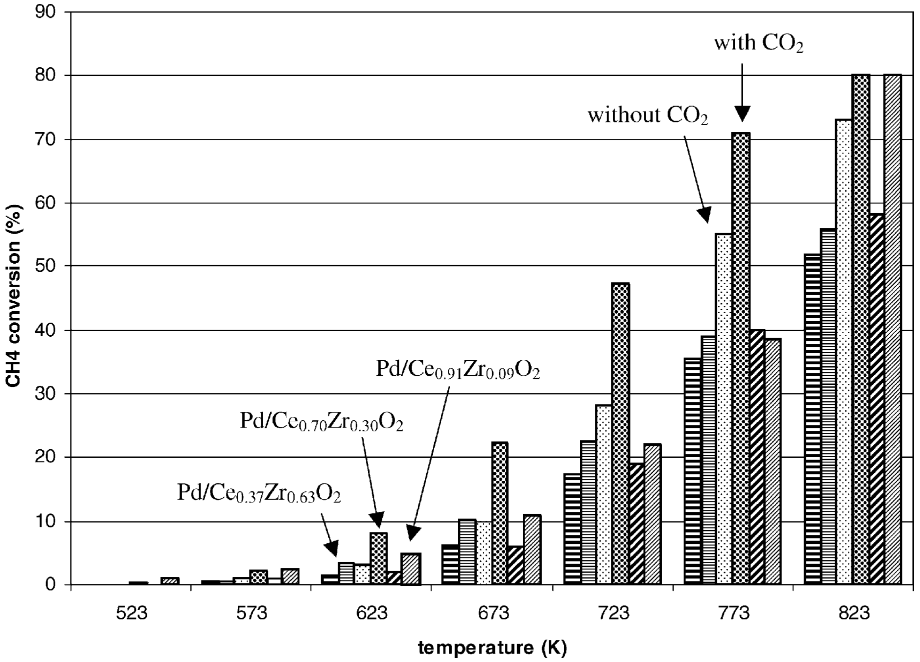

Fig. 1. Conversion of methane as a function of the temperature for palladium catalysts supported on ceria-zirconia mixed oxides. Horizontal lines represent the activity of $Pd/Ce_{0.37}Zr_{0.63}O_2$ catalyst, points are dedicated to the activity of $Pd/Ce_{0.70}Zr_{0.30}O_2$ catalyst and oblique lines are used for the activity of $Pd/Ce_{0.91}Zr_{0.09}O_2$. Spaced histograms figure the activity of those catalysts in the absence of CO_2 while the packed ones represent their activity in the presence of 3% of CO_2 in the reactants feed.

was higher for every catalyst in the presence of CO_2 at any temperature, except at 773 K for the palladium supported on $Ce_{0.91}Zr_{0.09}O_2$ mixed oxide, where the conversion remained unchanged. In terms of T_{50} values (temperature necessary to reach 50% of methane conversion), it appears that the addition of CO_2 allows to decrease this value by 10 K in the case of $Pd/Ce_{0.37}Zr_{0.63}O_2$ (808 K versus 818 K) and $Pd/Ce_{0.91}Zr_{0.09}O_2$ (788 K versus 798 K) and even by 35 K for the $Pd/Ce_{0.70}Zr_{0.30}O_2$ catalyst (728 K versus 763 K).

3.2. Characterisation of the catalysts

3.2.1. Addition of N_2O in the feed

Principal conclusions of these analyses are: (i) the fresh $NiMoO_4$ sample has a specific area value of 58 m^2/g. After the catalytic reactions in the presence or absence of N_2O, the specific area of $NiMoO_4$ drops very similarly for all tests to about 39 m^2/g. The surface area of α-Sb_2O_4 (1 m^2/g) remains unchanged after test. XRD patterns are the same, independently of the presence or absence of N_2O. The XPS results indicated that the binding energies are (almost) identical for the fresh $NiMoO_4$, α-Sb_2O_4, the mixture and the samples recovered after catalytic test. Ni/Mo XPS atomic ratio = 1.18, indicated an enrichment of the surface in Ni. The fresh $NiMoO_4$ and the $NiMoO_4+\alpha$-Sb_2O_4 mixture were fully oxidised (no Mo^{5+} is observed). There is no indication of carbide species of Ni or of Mo formed at the surface of the $NiMoO_4$ catalysts during the test. No significant differences in the atomic ratios were observed between the samples. A significant difference concerns the oxidation state of Mo. Mixtures are reduced after reaction. Indeed, XPS analysis showed that the quantity of Mo^{6+} decreases and that of Mo^{5+} increases in the presence of N_2O. For the $NiMoO_4$ and the mixture recovered after the addition of 300 ppm of N_2O, the amount of Mo^{5+} was about 0.3% of the total Mo. This suggests that, in the presence of N_2O, molybdenum is slightly reduced. More details can be found in [3].

3.2.2. Addition of CO_2 in the feed

XRD analyses are the same for catalysts in the presence and in the absence of CO_2. The BET surface area also remains unchanged. The XPS analyses of the samples after test, both with and without the addition of 3% of CO_2 into the feed, did not show any difference either in the binding energies (BE) of the different elements or in the Pd/(Ce+Zr) ratio. No carbide compounds were observed. However, interesting information comes from the analysis of the O 1s peak. Two kinds of oxygen O 1s species could be detected at the surface of the ceria-zirconia mixed oxide catalysts. The first one (low BE) is centred at around 529.5 eV and would be bound to Ce atoms whereas the other one (high BE) is located above 530.5 eV and is probably linked to other atoms like C or Zr. After reaction in the presence of CO_2, the proportion of low BE O 1s species seems to increase (between 3 and 17.5%) (Table 3). It is worth noting that this enhancement is more important on the most activated system by the presence of CO_2, i.e. the $Pd/Ce_{0.70}Zr_{0.30}O_2$ (about 20%). Similar conclusion is obtained if the amount of these low BE O 1s species is reported to the overall metallic content of the support.

3.3. Interpretation of the catalytic test

3.3.1. Addition of N_2O

The results observed with the mixture α-$Sb_2O_4+NiMoO_4$ are similar and confirm those observed with pure $NiMoO_4$. Under N_2O, molybdenum in $NiMoO_4$ works in a slightly more reduced state (XPS: presence of Mo^{5+}). Under these conditions, the catalyst is more selective. We have suggested that N_2O inhibits the adsorption of O_2, so limiting the oxidation rate of the catalysts [3,4]. This would account for the decrease in propane conversion, in O_2 consumption and in the yield in CO_2 observed in the mixture. When α-Sb_2O_4 is added to pure $NiMoO_4$ or when N_2O is introduced in the feed with pure $NiMoO_4$ (Tables 1 and 2), it is observed that the selectivity to propylene increases, the conversions of propane and of oxygen decrease and the yield in CO_2 decreases. These results could indicate that α-Sb_2O_4 and N_2O could probably play the same role, namely, controlling the selectivity of $NiMoO_4$ during the reaction, inhibiting non-selective sites. Previous studies [1] demonstrated that, working with pure molybdenum oxide (MoO_3), the key to maintain high catalytic performances (high selectivity in partial oxidation, low formation of CO_2) is to stabilise the surface of molybdenum oxide in a sub-oxide close to the stoichiometry of $Mo_{18}O_{52}$. This reduced state can be obtained when α-Sb_2O_4 is present in contact with MoO_3. Mars–van Krevelen mechanism considers that the hydrocarbon is oxidised incorporating oxygen from the outermost layer of the oxide, the oxide becoming reduced as a consequence.

Table 3
XPS results of various catalysts after test, both in the absence ($CH_4/O_2/He$ = 1/10/89, v/v/vv) and in the presence of 3% of CO_2 in the reactants mixture ($CH_4/O_2/CO_2/He$ = 1/10/3/86 v/v/v/v)

	Low BE O 1s/O (%)		Low BE O 1s/(Ce + Zr)	
	Without CO_2	With 3% of CO_2	Without CO_2	With 3% of CO_2
$Pd/Ce_{0.70}Zr_{0.30}O_2$	46.4	54.5 (+17.5)	1.67	2.02 (+21.0)
$Pd/Ce_{0.91}Zr_{0.09}O_2$	53.6	55.7 (+4.0)	2.16	2.31 (+7.0)
$Pd/Ce_{0.37}Zr_{0.63}O_2$	51.8	53.2 (+3.0)	1.26	1.25 (0.0)

Low BE O 1s = 529.5 eV. In parenthesis, change due to the introduction of CO_2, in %.

Molecular oxygen from the reaction gas then reoxidises the catalytic surface. It is well-established that, in general, the reoxidation step of the cycle is slower than the reduction one. Hence, the surface gets globally reduced with successive catalytic cycles. Pure MoO_3 undergoes a deep reduction and loss of activity. In the presence of α-Sb_2O_4, selectivity increases. The role of α-Sb_2O_4 is to irrigate the surface of MoO_3 with spillover oxygen which facilitates the oxidation of the surface of MoO_3 after incorporation of its oxygen atoms in oxidation products. During reaction MoO_3 in mixture with α-Sb_2O_4 is composed of a core of MoO_3 and a superficial layer possessing the stoichiometry of weakly reduced Mo ($Mo_{18}O_{52}$) [1]. Taking these results into account, it could be suggested that the role of N_2O could be the same. N_2O also facilitates the reduction of the surface of the molybdenum. But the mechanism by which the reduction of the catalysts is adjusted seems to be different. It could be suggested that N_2O inhibits the adsorption of oxygen on $NiMoO_4$, so promoting reduction. These results support the fact that a more reduced oxidation state of atoms at the surface of the catalysts could increase selectivity and that this state could be obtained by adding an oxide phase, which produces spillover oxygen or by adding N_2O as gas dope in the feed. The fact that there is no significant increase in the selectivity to propylene when N_2O is fed in the mixture of $NiMoO_4$ and α-Sb_2O_4 is coherent with this picture. In the mixture, the selectivity is already largely modulated by α-Sb_2O_4.

3.3.2. Addition of CO_2

The presence of some CO_2 in the feed allows the reaction of catalytic combustion of methane, on palladium supported on ceria-zirconia mixed oxide catalysts, starting at lower temperatures than what is observed in the absence of CO_2. XPS results seem to give an attempt of explanation for this activation in the presence of CO_2. According to the XPS results, there is an enrichment in low BE oxygen species of the ceria-zirconia compound when CO_2 is present. As a preliminary explanation, it could be suggested that these oxygen species would come from the dissociation of some CO_2 molecules at the surface of the catalyst, which furnishes some activated monoatomic oxygen species (O^*) which, in turn, could either help to oxidise the CH_4 molecules or improve the oxidation rate of catalysts by modifying its oxidation state and increasing the overall activity of the catalyst. Indeed, it has recently been shown, using Raman spectroscopy under *operando* conditions, that, in the case of Pd/Al_2O_3 catalysts, the most active catalyst is obtained when palladium is working in a highly oxidised state [7]. One should notice that the enhancement in low BE oxygen species is more important on the most activated system by the presence of CO_2 ($Pd/Ce_{0.70}Zr_{0.30}O_2$). This last observation seems to support our interpretation. However this observation has to be verified further. The observed effect of CO_2 could be in contradiction with previous results presented in the literature [5,8] which showed that CO_2 does not modify the catalytic performances of Pd/α-Al_2O_3 catalysts. The explanation of this apparent contradiction is that the role of CO_2 depends on the nature of the catalysts (more precisely on the nature of the support), as is discussed elsewhere [9]. The important point to underline is that CO_2 could be used to improve the efficiency of catalytic combustion and, thus, the energetic efficiency. This is a very new result, not yet published up to now.

4. Conclusions

The oxidation state of the catalysts can be tuned by adding small amounts of gas dopes in the reaction feed. The adjustment of the concentrations of N_2O and CO_2 thus clearly appears as a promising tool to modify the number of selective sites, to improve selectivity of partial oxidation products and to improve combustion of methane.

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References

[1] E.M. Gaigneaux, H.M. Abdel Dayem, E. Godard, P. Ruiz, Appl. Catal. A: Gen. 202 (2000) 265–283.
[2] F. Dury, E.M. Gaigneaux, P. Ruiz, Appl. Catal. A: Gen. 242 (2003) 187–203.
[3] F. Dury, M.A. Centeno, E.M. Gaigneaux, P. Ruiz, Appl. Catal. A: Gen. 247 (2003) 231–246.
[4] F. Dury, M.A. Centeno, E.M. Gaigneaux, P. Ruiz, Catal. Today 81 (2) (2003) 95–105.
[5] D. Ciuparu, E. Altman, L. Pfefferle, J. Catal. 203 (2001) 64–74.
[6] O. Demoulin, J.L. Mugabo, M. Navez, P. Ruiz, Appl. Catal. B: Environ., in preparation.
[7] O. Demoulin, M. Navez, E.M. Gaigneaux, P. Ruiz, A.-S. Mamede, P. Granger, E. Payen, Phys. Chem. Chem. Phys. 5 (2003) 4394–4401.
[8] R. Burch, P.J. Urbano, P.K. Loader, Appl. Catal. A: Gen. 123 (1995) 173–184.
[9] O. Demoulin, M. Navez, F. Gracia, E.E. Wolf, P. Ruiz, Catal. Today, submitted for publication.