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An attempt to explain the role of CO_2 and N_2O as gas dopes in the feed in the oxidative dehydrogenation of propane

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Abstract

Dynamic effects brought about by the introduction of small amounts of CO_2 and N_2O in the reaction feed during the oxidative dehydrogenation of propane to propene on α-$NiMoO_4$ catalysts are reported. CO_2 promotes oxidation probably via the formation of adsorbed oxygen species, O(a), formed by the dissociation of CO_2 on $NiMoO_4$. Catalysts in presence of CO_2 work in a high oxidation state increasing conversion. CO_2 is not an inert non-selective product. It can play an active role during the reaction. It could, via O(a): (i) oxidise propane to propene, (ii) increase the oxidation state on the surface of the catalyst and (iii) in high concentration, promote the non-selectivity of the catalyst. In presence of N_2O, catalytic sites work in a more reduced state. N_2O improves selectivity, probably by: (i) inhibiting the adsorption of O_2 and/or (ii) increasing reduction rate of the catalysts. The O^* produced by dissociation of N_2O can oxidise propane to propene. Adjusting the concentration of promoters could be an useful tool to modulate selectivity during the catalytic reaction.

Keywords: Oxidative dehydrogenation of propane; Nickel molybdate; CO_2 dissociation; Reactivity of CO_2; N_2O dissociation; Reactivity of N_2O; Dynamic control of active sites; Doping gas feed

1. Introduction

The addition of gas promoters is already used in some industrial applications. Gaseous dopes added to the reactant feed of a reactor could improve activity and selectivity and inhibit non-desirable reactions and deactivation. However, literature is scarce on the exact role that gaseous promoters play during the catalytic reaction. Fundamental studies are then of high priority in this field. A better understanding of the mechanistic processes in presence of dopes are then a key to understanding the real state of the catalysts during the reaction, and to improve selectivity. The possibility that co-adsorbate species could modify the intrinsic activity/selectivity of the surface and the pathways of transformation or could play a direct role as co-catalysts has been discussed based on indirect experimental evidence [1]. The partial oxidation of benzene to phenol on V, W, La, Mo, enriched with Pt or Pd catalysts was studied in the presence of a mixture of oxygen and hydrogen [2]. The direct oxidation of propylene to propylene oxide on Ti-catalysts was performed using hydrogen as a dope [3]. CO_2 has been used as a dope in the oxidation of alkylaromatics over

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Fe/Mo/borosilicate molecular sieve [4], in the synthesis of methanol from synthesis gas [5] and in the oxidative dehydrogenation of isobutane over LaBaSm oxide catalysts [6]. Recently, CO_2 has been claimed to be an effective dope in the oxidation of butane to maleic anhydride [7]. N_2O has been used as pure oxidant: in the oxidative coupling of methane to ethane [8] or formaldehyde [9,10], in the transformation of benzene to phenol [11] or in the oxidation of ethylene to epoxide [12,13].

Our work is based on the well established fact that the dynamic processes occurring at the surface of oxide catalysts during oxidation reactions could modify strongly the surface properties of the catalysts. The understanding of the role of promoters on the activity and selectivity of an oxidation process thus requires the knowledge of the effects induced by all the factors which could influence the architecture of the active sites and the dynamic phenomena occurring at the surface of the catalyst during the reaction.

The aim of the present contribution is to shed light on these aspects. It concerns the effects brought about by the introduction of small amounts of CO_2 and N_2O, in the feed during the oxidative dehydrogenation of propane. Our objective is not to design new performant catalysts but to detect any change or tendency in the catalytic performances due to the addition of small amounts of gas dopes. We have selected $NiMoO_4$ as catalysts. This catalyst (formed principally by α- and β-phase) shows interesting catalytic performances and a good selectivity. Experiments carried out by using $NiMoO_4$ in alkane oxidation have already shown that a molybdenum to metal (Mo/M) ratio greater than one, or, in other words, the presence of molybdenum oxide besides metallic molybdates, enhances its catalytic properties [14–20].

The strategy followed in this work is to carry out the reaction in presence and absence of CO_2 and N_2O and to characterise the catalysts before and after reaction in order to correlate the catalytic activity with any change occurring on the catalysts during the reaction and to determine the effect of the addition of dopes on such changes. It will be demonstrated that CO_2 and N_2O are able to modify the chemical state of the active sites of $NiMoO_4$ under the conditions of reaction and that the dissociation of both dopes on the surface of the catalyst have to be taken into account to explain the catalytic performances in their presence. Both dopes can oxidise the propane to propene.

2. Experimental

2.1. Preparation of catalysts

Nickel molybdate was prepared from a 0.0571 M aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot7H_2O$, Aldrich, >99%) and a 0.4 M aqueous solution of nickel nitrate ($Ni(NO_3)_2\cdot6H_2O$, Aldrich, >99%) (36). A 1000 ml volume of the nickel solution was heated to 333 K in a 2000 ml vessel. Then, 1000 ml of the ammonium heptamolybdate solution was added drop-wise to the nickel solution under vigorous stirring, maintaining the same temperature. The pH of the mixture was kept constant at a value of 6 by the addition of ammonium hydroxide. After 4 h, the reaction mixture was filtered and the precipitate was dried in air at 283 K for 24 h. It was thereafter calcined at 773 K for 4 h under 60 ml min^{-1} of flowing oxygen (Indugas, 99.995%).

2.2. Catalytic test

Catalytic tests were performed in a conventional fixed-bed micro-reactor (Pyrex U-tube with an internal diameter of 8 mm) operated at atmospheric pressure. The catalysts were used as pellets with a granulometry between 200 and 315 μm. The concentrations of both O_2 (Indugas, 99.995%) and propane (Indugas, 99.5%) in the feed were 10% by volume. Helium (Indugas, 99.995%) was used as carrier gas. The total flow of the reactant mixture was 30 ml min^{-1}. Catalytic activity was measured in the absence and in the presence of 3% CO_2 (Indugas, 99.998%) or 300 ppm N_2O (Indugas, 99.998%) introduced as gas dope in the feed. In order to maintain the space velocity constant for all tests, the flow of He was balanced so that the total gas flow was unchanged. In the case of addition of CO_2, the reaction was run at 673, 723 and 753 K for 2 h at each temperature. In the case of N_2O dope, temperature was 723 K. An additional experiment was also performed, stopping the feed in N_2O and maintaining the operation conditions unchanged. Analysis of reactants and products was continuously performed by on-line gas chromatography (GC) using two columns, namely a Hayesep Q column 1.5 m × 0.3 cm (100–120 μm) and a molecular sieve 1.5 m × 0.3 cm (0.5 nm). Carrier gas in both columns was helium. As the variation of performance with the introduction of dopes was not high, replicates of the catalytic reactions measurements under identical conditions and using catalysts from the same batch were performed to verify the results and to detect tendencies. The measured performances were accurate within about 1% (in relative) for the conversions of propane and oxygen and within 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).

2.3. Characterisation techniques

BET surface areas, were measured using a Micromeritics ASAP 2000 instrument by adsorption of nitrogen at 77 K on 200 mg of samples previously degassed at 423 K for 2 h under a controlled 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 $0.02^\circ\ \mathrm{min}^{-1}$. Identification of the phases was carried out by using JCPDS database.

XPS was performed with two different instruments depending on the samples. $NiMoO_4$ samples were analysed with a 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. Pass energy for the analyser was 50 eV and the spot size was 1000 μm in diameter, corresponding to a FWHM (full width at half maximum) of 1.1 eV for the Au $4f_{7/2}$ band of a gold standard. For these measurements, Ni 2p, Mo 3d, O 1s and C 1s bands were recorded. 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, Wagner sensibility factors were used. Decomposition of the Mo 3d doublets to Mo^{n+} species was done by fixing an energy gap of 3.15 eV, and an area ratio of 2–3 between the Mo $3d_{3/2}$ and the Mo $3d_{5/2}$ bands. Solutions of the decomposition were afterwards validated by checking that the binding energies for the different Mo^{n+} eventually found fitted with those commonly accepted and that an energy gap of about 1.2 eV existed between corresponding bands of two successive Mo^{n+} species.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were obtained by using a controlled temperature and environment reflectance cell (Spectra-Tech 0030-102) with ZnSe windows coupled to a Brucker EQUINOX55 infrared spectrometer equipped with an air cooled MIR source with KBr optics and a MCT detector. The sample was placed inside the chamber without packing or dilution. A flow of $36.4\ \mathrm{ml\ min}^{-1}$ of He was introduced in the DRIFTS cell during 1 h and the spectra of the original sample collected. Then the sample was heated "in situ" to 728 K under helium, maintained 1 h at such temperature and then 1% of N_2O, 10% of N_2O and then synthetic air (20% O_2 and 80% N_2) was adsorbed successively. All the experiments were carried out at $36.4\ \mathrm{ml\ min}^{-1}$ of total flow of reactants. Spectra were obtained by co-adding 200 scans at $4\ \mathrm{cm}^{-1}$ of resolution, and they are presented in absorbance mode without any manipulation.

NH_3-TPD was performed to determine the number and the strength of the acid sites. The samples were first degassed for 1 h at 743 K under helium. Thereafter, NH_3 (anhydrous, Indugas) was adsorbed on the samples at 423 K as 10 pulses of 380 μl. The desorption profile was recorded by GC–MS while heating the sample at a rate of $10\ \mathrm{K\ min}^{-1}$ up to 743 K and then stabilising it at this temperature for 30 min. The quantity of NH_3 adsorbed and that desorbed were both measured by titration of the ammonia trapped at the outlet of the reactor in a solution of boric acid.

Raman spectroscopy measurements were performed with a Labram spectrometer (Dilor) interfaced with an Olympus optical microscope. The excitation radiation was a He:Ne laser (632.8 nm) operated at a power of 10 mW. The 100× objective of the microscope was used so that a spot of about 1 μm at the surface of the sample was measured at once. Spectra were obtained by averaging three scans of the Raman shift range between 1200 and $200\ \mathrm{cm}^{-1}$ recorded in 10 s with a spectral resolution of $7\ \mathrm{cm}^{-1}$. The identity of the spectra obtained at different positions of each sample was systematically verified.

Table 1
Catalytic activity of $NiMoO_4$ catalysts (250 mg), in presence and absence (in parenthesis) of CO_2 as dope

T (K)	*X* C3 (%)	*Y* C3 (%)	*S* C3 (%)	*X* O_2 (%)	*Y* CO_2 (%)	*S* CO_2 (%)
673	5.9 (4.6)	1.9 (1.6)	32.9 (34.3)	13.4 (17.7)	1.6 (2.8)	27.9 (61.8)
723	15.1 (12.8)	3.5 (3.8)	22.9 (29.7)	42.5 (45.4)	5.0 (6.8)	32.8 (52.9)
753	21.9 (22.0)	4.6 (5.0)	20.9 (22.7)	67.0 (71.2)	9.0 (9.8)	41.0 (44.7)

Yield in CO_2 has been corrected subtracting the amount of CO_2 injected as dope. *X*: conversion, *Y*: yield and *S*: selectivity.

3. Results

3.1. Catalytic test CO_2 as a dope

With respect to the results obtained for the tests in the absence of CO_2, the consequences of the addition of CO_2 in the gas feed, which were verified in replicate experiments, are (Table 1): (i) an increase in the conversion of propane at 723 K (18%), an increase at 673 K and no change at 753 K, (ii) an increase in the yield of propene at low temperature (18%) and a decrease at high temperature (−8%), (iii) a decrease in the selectivity of propylene at all temperatures (−10% on average), (iv) a decrease in the consumption of oxygen at all temperatures (−10% on average) and (v) a decrease in the yield and selectivity in CO_2 (−26 and −38%, respectively, at 723 K). The addition of CO_2 in the feed also induces formation of a small amount of a non-identified oxygenated compound.

3.2. N_2O as a dope

The addition of 300 ppm of N_2O leads (Fig. 1) to: (i) a decrease in the conversion of propane (−15%), (ii) a modest increase in the yield in propene (11%), (iii) an increase in the selectivity in propene (32%), (iv) a weak decrease in the selectivity in CO_2 (−7%). Similar results are observed at all temperatures. An important fact is that when the feed in N_2O is stopped, the catalytic performance remains unchanged compared with that in presence of N_2O. The performances observed before the addition of N_2O are only slowly re-established.

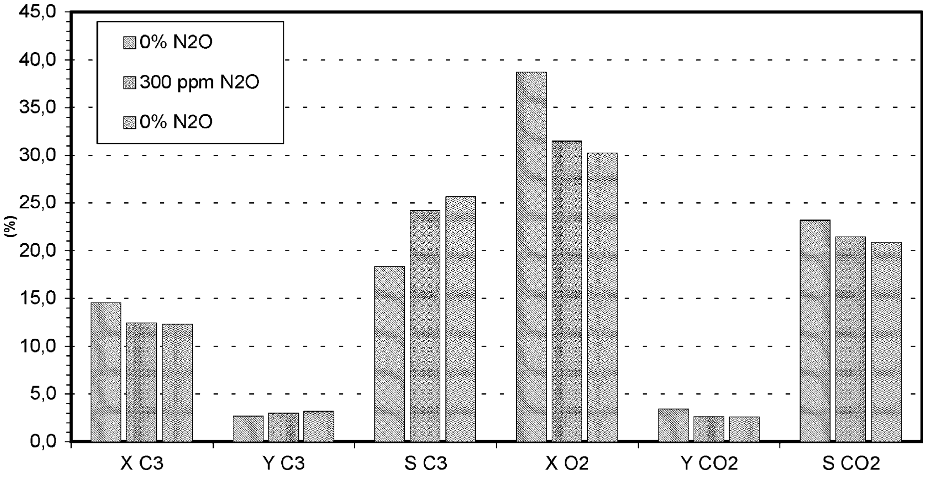

Fig. 1. Conversion of propane (*X* C3), yield in propene(*Y* C3) and selectivity in propene (*S* C3), conversion of oxygen (*X* O_2), yield (*Y* CO_2) and selectivity (*S* CO_2) in CO_2 obtained with 250 mg of $NiMoO_4$ at 723 K for the different catalytic tests made successively: (a) without N_2O; (b) same conditions as in (a) but in presence of 300 ppm of N_2O; and (c) same conditions as in (a) after stopping the feed in N_2O. The data plotted correspond to the performance obtained at the beginning of the test during the 1 h of reaction.

3.3. Characterisation

3.3.1. CO_2 as dope

The fresh $NiMoO_4$ sample has a specific area value of $58\,m^2\,g^{-1}$. After reaction in presence or absence of CO_2, the specific area of $NiMoO_4$ drops by about 40%.

Before reaction, the XRD pattern possesses all the peaks characteristic of α-$NiMoO_4$ [21,22]. Only two peaks, at 2θ values of 26.6 and 27.3°, do not belong to α-$NiMoO_4$, pointing to the presence of β-$NiMoO_4$ [21]. Independent of the conditions of reaction, the two peaks of β-$NiMoO_4$ almost completely disappear after catalytic test. This observation indicates without ambiguity that β-$NiMoO_4$ is not stable during any of the catalytic tests, regardless of the presence or absence of CO_2. The XRD peaks of the α-$NiMoO_4$ catalyst after both tests are completely identical to those found in the fresh sample. No new oxide phase was observed in any case.

The Raman spectrum found for the fresh $NiMoO_4$ exhibits a combination of peaks typical of Mo–O vibrations involving molybdenum atoms in an octahedral co-ordination (peaks at 938.1, 907.8 and $703.1\,cm^{-1}$) and of peaks typical of Mo–O vibrations involving molybdenum atoms in a tetrahedral co-ordination (peaks at 955.1, 885.7 and $818.2\,cm^{-1}$). Tetrahedral peaks were attributed to β-$NiMoO_4$ [22]. After the test with or without CO_2, all the peaks corresponding to tetrahedral co-ordinations have disappeared and only those corresponding to octahedral co-ordinations remain, identically to those found for the fresh $NiMoO_4$. This indicates that (i) the α-$NiMoO_4$ phase undergoes an oxidation of its structure during the tests performed both in presence or not of CO_2, (ii) the presence of CO_2 in the feed does not perturb this tendency and (iii) CO_2 succeeds in maintaining the structure of α-$NiMoO_4$ in a rather oxidised state during the catalytic reaction.

From XPS analysis it is concluded that all the binding energies corresponding to C, O, Mo and Ni are almost identical for the fresh $NiMoO_4$ and the samples recovered after the different catalytic tests (Table 2). In particular, no contribution in the C 1s signal for binding energies below 283 eV, attributed to carbide species, is found for any sample. Also, no significant differences in the atomic ratios are observed between the samples. The fact that the values for the Ni/Mo XPS atomic ratios are higher than 1 indicates an excess of Ni with respect to the stoichiometry at the surface of the $NiMoO_4$ samples. The increase of this ratio after reaction could be explained by the segregation of NiO particles towards the surface of α-$NiMoO_4$ during the catalytic reaction. For the fresh $NiMoO_4$, as for the catalysts recovered after both tests, only Mo^{6+} species are found [22].

Table 2
Atomic percentages and atomic ratios obtained by XPS for the $NiMoO_4$ fresh and after the catalytic tests in presence or absence of CO_2

	Fresh	After test in absence of CO_2	After test in presence of CO_2
C	18.3 (284.9)	19.5 (284.8)	21.6 (284.8)
O	53.7 (530.4)	52.1 (530.4)	51.6 (530.3)
Mo	12.0 (232.4)	11.7 (232.6)	12.5 (232.5)
With Mo^{6+}	12.0	11.7	12.5
With Mo^{5+}	0	0	0
Ni	16.0 (855.6)	16.7 (855.7)	14.3 (855.7)
C/Mo	1.5	1.7	1.7
O/Mo	4.5	4.5	4.1
Ni/Mo	1.3	1.4	1.1

Binding energies (in eV) are given in parenthesis.

DRIFTS spectra of the fresh $NiMoO_4$ sample obtained at room temperature presents the following bands in the region $760–1000\,cm^{-1}$: 1000, 976, 940, 885, 823, 810 and $760\,cm^{-1}$. In spite of the considerable discrepancy between the IR band positions reported in the literature for molybdenum oxide and molybdates [24,25], which makes difficult the assignment of these bands, the ones observed in our sample match the ones described by Mestl et al. [24] for mechanically activated MoO_3 which they ascribed to MoO_3 and molybdenum hydrate, suggesting that the nickel molybdate is covered by MoO_3.

The band at $1000\,cm^{-1}$ is assigned to the Mo=O fundamental stretching vibration of crystalline MoO_3 [24] and those at 976, 885, 823 and $810\,cm^{-1}$ are attributed to vibrations of the terminal Mo=O [25]. The existence of molybdenum hydrate can be postulated by the presence of the band at $760\,cm^{-1}$, ascribed to a Mo–OH stretch, and that at $955\,cm^{-1}$ [24,25]. When sample is heated to 728 K, a decrease in intensity of the bands due to MoO_3 is observed. This fact must be related with the thermal dehydration of the solid. No vibration band is ever found in the range

1450–1410 cm^{-1}, for any of the samples analysed, the fresh $NiMoO_4$ and the catalysts recovered after the different catalytic tests. This indicates that under the sets of conditions of reaction described in this work, carbonate species never form at the surface of $NiMoO_4$ [22].

Results from the ammonia TPD show that the fresh $NiMoO_4$ and the catalysts recovered after both tests adsorb similar quantities of NH_3 (about 2.0 μmol of NH_3 m^{-2}) at their surface. Also, TPD profiles are very similar for all the samples with the desorption starting around 483 K, then suddenly increasing to reach an identical maximum between 543 and 563 K, before slowly decreasing linearly until about 783 K [22].

3.4. N_2O as dope

The drop in specific area of $NiMoO_4$ is very similar to that of the test in presence of CO_2. XRD patterns after catalytic test are similar to that of the fresh catalyst, whether the reaction is performed in presence or in absence of N_2O. The peaks corresponding to β-$NiMoO_4$ disappear after catalytic test. No new peak is observed [23].

The Raman spectra for catalysts, fresh and after reaction, in presence or in absence of N_2O, are essentially the same. Spectra after reaction present only the octahedral co-ordination peaks. The peaks corresponding to molybdenum in tetrahedral position disappear after a catalytic test [23].

The XPS analysis results are essentially the same as those observed in the presence of CO_2, except that, comparing with fresh catalysts, after reaction in presence of N_2O, the amount of Mo^{5+} increases. Reduced molybdenum is observed. The reduction of molybdenum atoms seems induced by the presence of N_2O during the reaction. On the other hand, the C/Mo and the O/Mo XPS atomic ratios remain nearly unchanged (Table 3) [23].

Table 3
Atomic percentages and atomic ratios obtained by XPS for the $NiMoO_4$ fresh and after the catalytic tests in presence or absence of N_2O

	Fresh catalysts	After test in absence of N_2O	After test with 300 ppm N_2O
C	18.3 (284.8)	19.5 (284.8)	20.3 (284.9)
O	53.7 (530.4)	52.1 (530.4)	52.7 (530.6)
Mo	12 (232.4)	11.7 232.6)	12.8 (232.7)
With Mo^{6+}	12	11.7	12.5
With Mo^{5+}	0.0	0.0	0.3
Ni	16.0 (855.6)	16.7 (855.7)	14.3 (855.8)
C/Mo	1.5	1.7	1.6
O/Mo	4.5	4.5	4.1
Ni/Mo	1.3	1.4	1.1

Atomic ratio. Binding energies (in eV) are indicated in parenthesis.

Results from TPD-NH_3 showed that desorption profiles are essentially similar for fresh and used samples, in presence or absence of N_2O (as in the case of the presence of CO_2) [22,23].

Fig. 2 shows the different DRIFTS spectra of the $NiMoO_4$ solid at 728 K under 1% N_2O, 10% N_2O, Helium and synthetic air flow against the initial spectrum under helium at the same temperature. The introduction of 1% N_2O in the DRIFTS cell (Fig. 2, trace C) induces an increase in the intensity of the bands of the molybdenum–oxygen vibrations in the 1100–500 cm^{-1} region. Simultaneously, a decrease in the intensity of the bands due to stretching and bending modes of hydroxyls groups are produced (not shown). However, no bands assigned to the adsorbed N_2O species are detected, and only gaseous N_2O bands are visible. A similar behaviour is observed when increasing the concentration of N_2O in the gas phase to 10% (Fig. 2, trace B). It is clear that gaseous N_2O is able to interact with the surface OH groups of $NiMoO_4$, inducing changes in the metal–oxygen structure. When N_2O is removed from the gas phase, reverse changes in the DRIFTS spectra are observed. However, it is important to note that this is not a completely reversible process, since the band intensities of the initial spectra are not fully recovered (Fig. 2, trace D). The introduction of synthetic air in the DRIFTS chamber has a similar but deeper effect on the spectra than the one described for N_2O. Three observations and/or conclusions must be extracted from this figure: (i) N_2O and air exert a similar effect on the DRIFTS spectra, increasing the intensity of the Mo–O vibrations bands; (ii) such effect is not fully reversible, as can be deduced from the remaining positive intensity of the Mo–O bands after removing N_2O from the chamber and (iii) the intensity of the bands due to Mo–O vibrations of the solid increases in the sequence: Helium < 1% N_2O < 10% N_2O < synthetic air. From these results it could be concluded that N_2O promotes less amounts of metal–oxygen structure than oxygen(air), namely a more reduced oxidation state

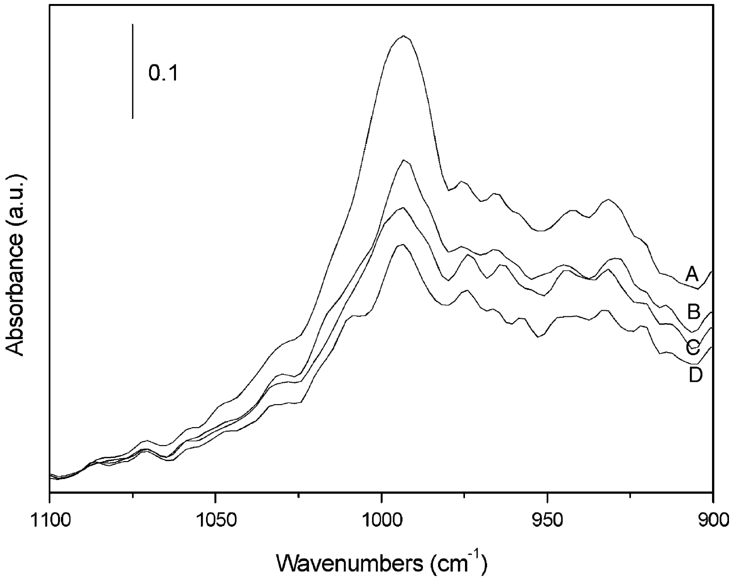

Fig. 2. Difference DRIFTS spectra of the $NiMoO_4$ solid at 728 K under different atmospheres, against the initial spectrum under helium. (A) Synthetic air; (B) 10% N_2O; (C) 1% N_2O; and (D) helium flow.

of molybdenum on $NiMoO_4$ solid [23] is established under N_2O flow than under oxygen (air).

4. Discussion

4.1. The architecture of Ni molybdate

The fresh nickel molybdate sample has an XRD pattern possessing all the peaks characteristics of α-$NiMoO_4$. Only two peaks can be attributed to the presence of β-$NiMoO_4$. The presence of β-$NiMoO_4$ is additionally suggested by Raman spectroscopy. The DRIFTS experiments seem to point to the presence of pure MoO_3. No bands attributed to molybdates or other Ni compounds were observed.

The most plausible architecture for the fresh $NiMoO_4$ sample consists in a mixture of α-$NiMoO_4$ phase, as the main component, and of β-$NiMoO_4$ phase as a minor component, probably both covered on the surface by small amounts of MoO_3 crystallites. In presence or absence of dopes, β-$NiMoO_4$ phase completely disappears after catalytic test. This observation indicates without ambiguity that β-$NiMoO_4$ is not stable during the catalytic tests, regardless of the presence or absence of dopes. The Raman spectrum found for the fresh $NiMoO_4$ exhibits a combination of peaks typical of Mo–O vibrations involving molybdenum atoms in an octahedral co-ordination and in a tetrahedral co-ordination. Peaks corresponding to octahedral co-ordinations are more intense than those corresponding to tetrahedral co-ordinations and are characteristic of the α-$NiMoO_4$ phase. The peaks in tetrahedral co-ordination are situated on reduced α-$NiMoO_4$ matrix and on β-$NiMoO_4$ phase [22]. After the tests in presence or absence of dopes, all the peaks corresponding to tetrahedral co-ordinations have disappeared and only those corresponding to octahedral co-ordinations are observed.

4.2. Attempt to explain the effects due to the introduction of dopes

It is evident that adding certain amounts of CO_2 or N_2O in the feed produces important changes in the catalytic activity. Data from the characterisation exclude that the observed catalytic effects could be explained by: (i) a change in the surface area, in fact in presence and in absence of dopes the changes in BET surface area are exactly the same, (ii) the formation of a new compound: although the crystallographic phases change during the catalytic reaction, the evolution of the phases observed by XRD are the same whether dopes are present or not. We remark that in all cases the formation of a carbonate, nitrate phase or other mixed oxide is excluded, (iii) a change in the acidity: the results on TPD of ammonia are very conclusive: the acidity in any case is the same. The acidity of the catalysts is not modified by the presence of dopes.

The XPS results clearly show that, compared with catalysts having worked in absence of dopes, N_2O promotes the reduction of the catalysts. On the contrary, in presence of CO_2 the catalysts work under a more oxidised state. In presence of both dopes, changes in the surface are not significant, except the decreases in the Ni/Mo atomic ratio which is easily explained by a preferential deposition of carbonaceous species on Ni atoms. As a consequence of all of this, the most likely explanation of the observed catalytic results is that both dopes succeed in modifying principally the chemical state of the active sites of $NiMoO_4$ under the conditions of reaction. Our suggestion is that the mechanism by which such modification is realised is via the dissociation of both dopes on the surface of the $NiMoO_4$.

4.3. Explanation of the effects observed in presence of CO_2

Two arguments point to an oxidating role of CO_2: (i) XPS indicates that the catalysts are not reduced in presence of CO_2 and (ii) Raman microscopy shows that, as in absence of CO_2, the tetrahedral species disappear after reaction. A crucial experiment to prove the oxidating role of CO_2 was performed reacting a reduced molybdenum phase (namely Mo_8O_{23}) with O_2 or with CO_2, under exactly the same reaction conditions. Catalysts were analysed by XPS under very sensitive conditions [22]. The main contribution of the Mo 3d band for the fresh Mo_8O_{23} corresponds to Mo^{6+} species. An Mo^{5+} contribution is also found representing about 11% of the total molybdenum. When Mo_8O_{23} is submitted to a flow of diluted O_2 at 673 K, its surface undergoes oxidation, verified by a lower proportion of Mo^{5+} found at its surface. However, the proportion of Mo^{5+} species decreased also when Mo_8O_{23} was submitted to a flow of diluted CO_2. More surprisingly, in this last case the amount of Mo^{5+} is slightly smaller than when the sample is oxidised using O_2. This shows without ambiguity that CO_2 is able to oxidise the reduced Mo_8O_{23} and, in addition and unexpectedly, that it works more efficiently than O_2. To our knowledge, this is the first time that this type of result is presented in the literature.

The difficulty is that thermodynamics shows that the gas phase dissociation of CO_2 to CO and O_2 is very difficult or, more precisely, that it can be excluded, especially at the low temperatures used in this work [22]. That is the reason why we suggest that the mechanism by which CO_2 promotes such oxidation is via the formation of monoatomic oxygen species O(a) adsorbed on the surface of $NiMoO_4$. This species would form by the dissociative adsorption of CO_2 on the surface of $NiMoO_4$ following the reaction $CO_2 \rightarrow CO + O(a)$. Thermodynamics calculations shows that the dissociative adsorption of CO_2 to CO and O(a) on Ni catalysts should proceed spontaneously under our conditions of reaction. The free energy of formation of O(a) was indeed evaluated to be $-240\,\mathrm{kJ\,mol^{-1}}$ at 423 K [5]. We have no proof that such dissociation occurs in our catalyst, however the dissociation has been verified experimentally in the case of Ni, Pt, Cu catalysts by several physico-chemical methods (LEED, TDS, HREELS, TAP, etc.) [26–32]. This is an important argument which seems to support our hypothesis.

An attempt to detect CO production resulting from the dissociative adsorption of CO_2 was made. Regarding the sensibility of our equipment, no carbon oxide was detected. This clearly suggests that the dissociation of CO_2 under our experimental conditions is very low. In spite of that, the effect of such dissociation can be very important.

If this occurs, our results (XPS) show that one of the roles of O(a) would be to maintain the molybdenum sites in a high oxidation state during the reaction. However, we cannot exclude that O(a) is also directly involved in the oxidation of propane, as a reactant. To further understand the oxidating role played by CO_2, an additional test was performed with only a small amount of O_2 (0.5% by volume). A test was carried out in the absence of CO_2 (TABSCO2) and another one was carried out by adding 10% by volume of CO_2 (TWITHCO2). In TABSCO2, $NiMoO_4$ exhibits during the 1 h of reaction an extremely high conversion of propane (about 80%). Catalyst is very active but not selective. Propene is not formed at all and only a small amount of CO_2 is produced. Propane is principally decomposed into coke [22]. Other cracked and/or oxygenated compounds seem to be produced (they have not been identified successfully). After 1 h of reaction under these conditions, the catalyst deactivates suddenly and its conversion of propane drops completely to zero. When CO_2 (10% in volume) is added in the feed (TWITHCO2), propane is effectively converted, although the conversion is low (about 2%), and propene is produced with a high selectivity (around 66%), then the yield in propene is not negligible (about 1.3%). Moreover, contrary to the behaviour observed in test TABSCO2, $NiMoO_4$ does not undergo any deactivation with time-on-stream. In TWITHCO2, catalyst keeps its performances constant for several hours of reaction. No coke is formed. These results show unquestionably that CO_2 is able to oxidise propane to propene. Interestingly, these results are a good basis to explain the higher performances obtained by oxidising butane to maleic anhydride in presence of CO_2 [7].

However, the catalytic test in Table 1 give another insight. When the temperature is low (673 K), an increase in the propene formation is observed when adding 3% CO_2. This indicates that probably, under these conditions, the selective oxidation of propane is favoured. When the temperature increases, the increase in the conversion is not followed by an increase in the yield of propene, indicating that under these conditions the oxygen species formed is too active and selectivity is not favoured. This could indicate that under more drastic conditions (high temperature, high CO_2 concentration), the oxygen generated by the dissociation of CO_2 could lead either to promote the formation of non-selective sites or to oxidise non-selectively the propene. This result could have implications in the control of the processes due to the non-selective reactions (run-away in industrial oxidation reactions).

4.4. The role of N_2O

4.4.1. Modification of the surface atomic concentration during the reaction

The possibility of a modification in the surface composition of the catalyst due to a metal migration during the reaction seems to be excluded. Probably, carbonaceous products seem to be formed preferentially on Ni atoms, decreasing the Ni concentration on the surface, as is clearly indicated by XPS analysis. The decrease of Ni/Mo XPS atomic ratio is coherent with this picture. The weak decrease in the O/Mo XPS atomic ratio could be explained by the reduction of the catalyst due to the presence of N_2O, as discussed previously. However, the same decrease is observed in presence of CO_2. What is important to underline here is that it should not be necessary to call to some atom migration occurring on the surface due to the presence of N_2O to explain the observed results. In fact it would be very speculative to admit that by the only presence of N_2O in the feed, such migration could occur.

4.5. Dynamic processes involved under reaction conditions

As has been said previously and taken into account in the above discussion, the most likely explanation for the observed results is that the N_2O introduced in the feed is able, as CO_2 does, to modify the chemical state of the active sites on $NiMoO_4$ by some dynamic processes induced under the reaction conditions.

XPS give the argument for a plausible explanation. In the presence of N_2O, molybdenum works in a more reduced state (Table 3). Mo^{5+} is observed only in the presence of N_2O. The presence of 300 ppm of N_2O in the feed, promotes the reduction of molybdenum. Contrarily, in the absence of N_2O, no reduced molybdenum was observed. DRIFTS experiments strongly support this result. When N_2O is added, hydroxyls decrease and the bonds corresponding to M=O increase further. This indicates, unequivocally, that the interaction of N_2O with $NiMoO_4$ modifies the nature of the sites on the surface of the catalysts, decreasing the OH and promoting the formation of M=O bonds. When O_2 is introduced, after evacuation of the N_2O, the amount of M=O bonds formed increases further (Fig. 2). This indicates that the number of M=O bonds in presence of molecular oxygen is higher compared with those observed in presence of N_2O [23]. In other words, the surface of the catalysts is in a higher oxidation state in presence of O_2. On the contrary, when N_2O is added, the oxidation of the surface is limited, it is less oxidised. These results allow to suggest that, during the reaction in presence of N_2O, the catalyst is not able to reach an oxidation state as full as in its absence. In conclusion, N_2O inhibits the oxidation, promoting a more reduced oxidation state of the catalyst.

4.6. Mechanism by which N_2O limits the oxidation rate

It could be suggested that N_2O limits the oxidation rate of the catalysts by inhibiting the adsorption of O_2 on their surface. N_2O can be adsorbed in the same vacancies as O_2. There exists, then, a competition for the adsorption sites. The inhibition in the adsorption of O_2 can have two consequences: (i) to limit the amount of O^{2-} species produced by the dissociation of O_2 on the surface and/or (ii) to limit (or inhibit) the formation of more electrophilic oxygen species (O^-, and $O_2{}^-$) which can be formed from the dissociation of molecular oxygen on the $NiMoO_4$. This proposed mechanism of inhibition seems to explain correctly the results observed when 300 ppm of N_2O is added in the feed. It is observed that the conversions in propane and in oxygen decrease, the yield in propylene is little higher and the selectivity in propylene increases significantly (32%). In addition, the yield and the selectivity in CO_2 decrease. These results could be well explained admitting that some non-selective sites (where (non-selective) electrophilic oxygen species are formed) have been inhibited, then the conversion decreases and the consumption of oxygen decreases also. What is remarkable is that, in presence of N_2O, the amount of Mo^{5+} (and very probably the amount of M=O, following DRIFTS analysis) is higher than in the presence of O_2. This indicates that a more reduced oxidation state of molybdenum (and logically less amount of M=O) is the key point to control the selectivity of the catalyst and that this modulation of the oxidation state is realised by N_2O during the catalytic reaction. Briefly, N_2O inhibits the adsorption of O_2, so limiting the oxidation rate of the catalysts. Catalysts containing less oxidised sites work better than fully oxidised catalysts. The degree of reduction of the catalytic sites, thus their selectivity, can be controlled by adding N_2O in the feed. In other words, N_2O "creates" or "modulates", during the reaction, selective sites on the surface of the $NiMoO_4$.

4.7. Reversibility of the sites created by N_2O

Another important aspect that deserves attention is the fact that the catalytic performances observed in presence of N_2O, remain when the amount of N_2O is stopped. The effect produced by N_2O is reversible, but the reversibility is not instantaneous after the replacement of N_2O by O_2 in the feed. This has been observed clearly in DRIFTS experiments. The changes in the intensity of the bands associated to Mo=O induced by the introduction of N_2O in the DRIFTS cell remain, to a certain degree, up to 2 h after N_2O has been replaced by synthetic air (Fig. 2). This indicates that the nature of the selective sites created by N_2O is not modified spontaneously when the N_2O is not present any more in the feed. Namely, in spite of the absence of N_2O, the sites remain in their oxidation state which is adequate to produce propene from propane. Some time (probably hours) is needed to equilibrate the catalysts under the new reaction conditions. This result explains why it is necessary to maintain some amounts of N_2O in the feed to maintain the selective sites created during the introduction of N_2O [23].

4.8. The oxygen species formed by dissociation of N_2O

The nature of the oxygen species formed on the surface of the catalyst by dissociation of N_2O has been studied extensively using surface potential measurement on MoO_3/SiO_2 catalysts [10]. At lower temperatures (413–553 K) and in N_2O atmosphere, N_2O is decomposed following the reactions:

$$N_2O + e^- \rightarrow N_2 + O^-$$

$$O^- + e^- \rightarrow O^{-2}$$

This indicates that under the reaction conditions used in our work and under steady-state conditions, the two oxygen species can coexist on the surface. However, the amount of O^{2-} on the surface is probably low. As the O^- species leads to total oxidation products while the O^{2-} leads to selective oxidation products, it could be suggested that the presence of O^{2-} species, could be the responsible for the observed effects. Anyway, we cannot exclude that the dissociated oxygen (named O*) could participate directly as oxidating reactant producing oxygenated products or more precisely propene. This has been verified working under high concentration of N_2O. In fact in absence of oxygen, N_2O (10% in volume) is able to produce a conversion of propane of 8.5%, propene in appreciable yield (2.4%) with a higher selectivity (28.7%) while in presence of oxygen (5% in volume (namely the same amount of oxygen atoms)), a conversion of 10% with a yield of 2.1% and a selectivity of 20.6 is observed. This result shows without discussion that N_2O could be also an oxidant to produce propene.

5. Conclusions

Both CO_2 and N_2O succeed in modifying the chemical state of the active sites of $NiMoO_4$ under the conditions of reaction. CO_2 increases the oxidation state of Mo at the surface of the catalyst. The mechanism by which CO_2 promotes such oxidation goes via the formation of oxygen species on the surface (O(a)). This species would form by the dissociation of CO_2 on the surface of $NiMoO_4$. O(a) is more active as oxidant than O_2. The stronger oxidating character of O(a) is also consistent with the lower selectivity of the process (oxidation of selective products) and with the lower O_2 consumption (as part of the oxygen atoms come from CO_2 and no more only from O_2). A crucial implication of our results is that, contrary to what it is believed, CO_2 is not inert in the reaction. It is not only a non-selective product but it also modifies, via O(a), the selectivity of the catalyst.

In the presence N_2O, catalytic sites work in a more reduced state. N_2O inhibits the adsorption of O_2, so limiting the formation of non-selective oxygen species (from O_2) and/or the oxidation rate of the catalysts. This explains the increases in the yield and selectivity to propene and the lower O_2 consumption when N_2O is added. It is not excluded that N_2O (via the dissociated oxygen species O^*) could also participate directly as oxidant. If this is the case, the results, in particular at high N_2O concentration, must thus be regarded as due to the superposition of both above described phenomena.

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