ISOTHERMAL REDUCTION BEHAVIOUR OF SOME METAL MOLYBDATES
Selective light alkane oxydehydrogenation and/or olefins partial oxidation

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Abstract

The reduction profile of several unpromoted and promoted metal molybdate catalysts was investigated correlating their reducibility with the reactivity in catalysis.

Using the stoichiometric α- and β-nickel molybdate compounds it was observed that the reduction rate was significantly affected by the nature of the phase. The results show that β-NiMoO$_4$ phase led to a significant increase in the reduction rate with respect to α phase. The increased resistance to reduction by hydrogen due to the structure of the catalytic system is reported. It was found that there is a relationship between the reducibility of the catalysts and selectivity to dehydrogenation products, indicating that the lattice oxygen plays an important role in the reaction.

The effect of MoO$_3$, TeO$_2$ and Te$_2$MoO$_7$ added to NiMoO$_4$ systems on the reducibility of the catalyst and on the propylene oxidation were also studied. It was observed that the reduction rate was significantly affected by the nature of the doping element. The results show that NiMoO$_4$–MoO$_3$ combination led to a significant increase of the reduction resistance of the nickel molybdate while TeO$_2$ or Te$_2$MoO$_7$ addition increases its oxygen depletion rate. Ni–Mo–O systems (Mo/Ni>1) were found to favour low CO$_x$ selectivity, high selectivity to C$_3$H$_4$O and C$_3$H$_4$O$_2$ and good propylene conversion. In presence of TeO$_2$ and Te$_2$MoO$_7$ doped Ni–Mo–O system both acrolein and propylene conversion were increased with respect to the undoped system. Ni–Mo–Te–O catalysts have been found to have a reducibility trend which fits well with the acrolein and acrylic acid formation from propylene oxidation in presence of molecular oxygen.

Keywords: catalysis, isothermal reduction, metal molybdate catalysts, reducibility

Introduction

Metal molybdates are of great interest in heterogeneous catalysis and in industrial application. One important aspect of the chemistry of these compounds is their thermal behaviour, lattice oxygen mobility and structure defects [1–4]. Specifically the metal–oxygen bond strength vary depending on the nature and on the structure of the compound. Among the frequent catalysts used there is AMoO$_4$, A$_2$MoO$_7$, MoO$_3$, A$_x$(MoO$_4$)$_y$ (A: Ni, Co, Fe, Te, Zn, Mg, Bi) and their combination. Generally, the dif-

ficulty to remove oxygen from the lattice of a solid is even related to the strength of metal–oxygen bond. This feature can be evaluated by reduction potential or by re-oxidation heat. The weaker is the strength the easier is the lattice oxygen mobility and vice versa. However, in oxidation reactions, it is generally observed that the activity and selectivity of an oxide are related to its reducibility.

In this work we investigate the reduction profile of several unpromoted and promoted metal molybdate catalysts correlating their reducibility with the reactivity in catalysis.

Experimental

Catalysts preparation

The precursors are prepared by coprecipitation using a Mettler RC1 Reaction Calorimeter, which allows a careful control of the main experimental parameters (T, stirring speed, pH etc.) which determine the structure and surface characteristics of the active catalysts [5, 6].

$NiMoO_4$–MoO_3

The catalyst xNiMoO$_4$–yMoO$_3$ $0<y/x<5$ is prepared by coprecipitation from an equimolar molybdic acid (Aldrich) and nickel nitrate (Fluka) solution (0.25 M), at 85°C with the pH adjusted at 5.25 by addition of ammonia. When the precipitation is complete, the temperature of the solution is maintained at 85°C for stoichiometric (Mo/Ni=1) precursor formation while it was lowered to 65°C for the surstoichiometric (Mo/Ni>1) precursor formation. The precipitate is hot filtered at the same temperature, washed several times with hot distilled water, dried at 120°C for 15 h [5] and finally heated 2 h at 550°C. The catalyst particle size is 200–325 mesh.

Te_2MoO_7

Te_2MoO_7 is prepared by dissolving a mixture of ammonium heptamolybdate and telluric acid H_6TeO_6 under stirring in a minimum of distilled water and by heating progressively in order to concentrate the solution until a viscous white paste is obtained. The latter is then dried at 120°C for 15 h, ground and heated 2 h at 470°C. Te_2MoO_7 obtained (specific surface area 1 m^2 g^{-1}) has been characterised by XRD and IR techniques.

Te_2MoO_7/$NiMoO_4$–MoO_3

Doping with tellurium based oxide is performed by mechanical mixture of $NiMoO_4$–MoO_3 with Te_2MoO_7 (A). Alternatively tellurium molybdate is progressively formed by mixing telluric acid with $NiMoO_4$·MoO_3 (B). In this case H_6TeO_6 reacts with MoO_3 to form Te_2MoO_7 during the oxygen activation of the catalyst for 1 h. In both cases Te_2MoO_7/$NiMoO_4$·MoO_3 is formed. Catalyst runs were performed using both systems and the results reported where those obtained with (B) catalyst.

$P_2O_5/NiMoO_4–MoO_3$

Ni–Mo–O catalyst was impregnated with $(NH_4)_2HPO_4$ by using the incipient wetness technique and activated at 480°C for two h. The composition of the final catalyst was $[NiMoO_4]_x[MoO_3]_y[P_2O_5]_z$ with y/x=0.5 and z=0.04. When using the P-doped catalyst in the presence of water vapour, it is necessary to preliminarily activate the catalyst under the same reaction conditions for about 40 h in order to stabilise the activity of the catalyst.

Characterisation

Thermal studies of the catalysts were carried out on a Seiko TG-DTA instrument. With weighed samples (ca 20 mg) placed in alumina crucibles the reduction tests have been carried out isothermally (ITR isothermal reduction) under a hydrogen atmosphere (gas feed 6 L h^{-1}) while recording TG and DTG curves. The samples were preheated in helium up to the reduction temperature (T_r) before their reduction. Due to the coke formation, the hydrogen has been used instead of propane and the temperatures were kept lower than the catalytic reaction temperatures due to the higher reactivity of hydrogen with respect to hydrocarbons.

B.E.T. surface areas were measured using a Quantasorb Quantachrom instrument.

Some physico-chemical properties of the studied systems were reported elsewhere [7].

Activity tests

Catalytic runs were performed in the temperature interval 400–550°C using a quartz tubular reactor 50 cm long with an internal diameter of 8 mm. The catalyst was diluted with silicon carbide in order to prevent severe temperature gradients; the partial pressure of the alkanes or alkenes and oxygen in the gas feed was varied between 7 and 15% and between 2 and 18% respectively, using helium or nitrogen as diluent with a total feed ranging from 5 to 20 L h^{-1}.

The reaction products were analysed by gas chromatography: oxygen and carbon monoxide by a molecular sieve 5 Å, carbon dioxide by a Poropak QS column both connected to a T.C. detector. The propane, propylene, ethylene, acetaldehyde, acrolein and acrylic acid were separated and analysed by Porapak QS column linked to a F.I. detector.

Results and discussion

Metal molybdates are prepared by thermal treatment of their solvates, obtained by reaction of the corresponding nitrates with ammonium heptamolybdate or molybdic acid in aqueous solution. Particularly the stoichiometric nickel molybdate exists in two modifications at atmospheric pressure [5], i.e. the phase α, stable at room temperature, with molybdenum in a distorted octahedral site and the high-temperature phase β, with molybdenum in a distorted tetrahedral environment.

The primary goal of this research was to prepare metal molybdate based catalysts, which are of great importance in oxydehydrogenation of light alkanes into the corresponding alkenes and/or oxidation reaction of alkenes to oxygenates compounds, and to study their catalytic properties in relation with their thermal behaviour in reducing atmosphere. For this purpose, we studied the mutual influences of the co-cations 'A' on molybdenum oxygen bonds in the different structure such as $AMoO_4$ and A_2MoO_7, and also the synergetic effect of mixed oxides such as $NiMoO_4$–$xMoO_3$, $NiMoO_4$–TeO_2, $NiMoO_4$–Te_2MoO_7, $NiMoO_4$–$xMoO_3$–P_2O_5 and $NiMoO_4$–$xMoO_3$–Te_2MoO_7 in terms of lattice oxygen mobility. More specifically when two phases exist for the same catalyst (α and β phase of $NiMoO_4$ system) the interaction of hydrogen with the lattice oxygen of the two phases is investigated.
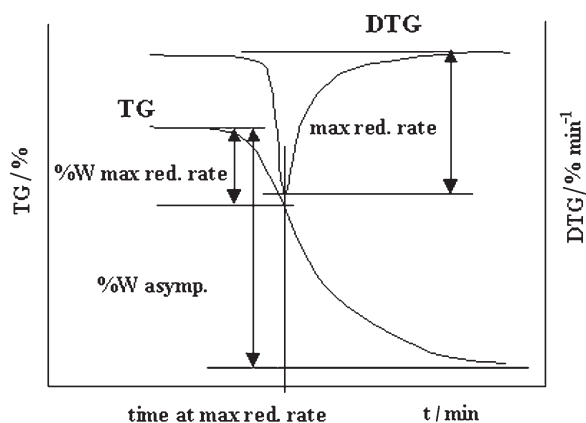

Fig. 1 Illustrative definitions of reduction rates of solids calculated from experimental TG- DTG-DTA curves obtained under H_2

The behaviour of the single or mixed molybdates during thermal reduction and consequently their activity, can be better understood if the decomposition patterns of the simple nickel, tellurium and molybdenum oxides are taken into account. The starting materials employed for the preparation are the same as reported in the experimental section. In order to describe the reduction profile of the solids studied and to evaluate their reduction rate an illustrative Fig. 1 is reported.

NiO, TeO₂ and MoO₃ reduction

The oxides were prepared from their respective salts by thermal treatment at high temperature and were then reduced isothermally with temperatures ranging from 440–520°C. Table 1 shows the effect of temperature on depletion rate of the solids. For the temperature of 440°C it can be seen that while nickel oxide presents a high reduction rate ca 5.46% min^{-1} i.e. 0.255 oxygen atoms min^{-1}, tellurium and molybdenum oxides remain unaffected under these conditions. Their reducibility increases with temperature (Table 1, Figs 2 and 3).

Catalyst formulation	T of reduction/ $C°$	Mass asymptotic loss/%	Oxygen atoms lost/ atom/formula	Max reduction rate/ mass% min^{-1}	Max reduction rate/ oxygen atom min^{-1}	Mass loss at the maximum reduction rate/%	Oxygen lost at the maximum reduction rate/atom/ formula
(1) α-NiMoO$_4$	441.5	19.1	2.61	0.984	0.134	11.1	1.52
(2) β-NiMoO$_4$[*]	442.2	22.8	3.12	1.305	0.178	4.4	0.60
(3) Ni$_{0.9}$MoO$_{3.9}$	443.0	20.6	2.72	1.053	0.139	5.6	0.74
(4) NiMoO$_4$–0.5MoO$_3$	440.5	22.0	4.00	1.420	0.258	6.0	1.09
(5) NiMoO$_4$–MoO$_3$	441.3	18.0	4.08	0.642	0.145	4.6	1.04
(6) NiMoO$_4$–5MoO$_3$	442.2	11.1	6.51	0.200	0.117	3.4	1.99
(7) NiMoO$_4$–0.5MoO$_3$–0.04P$_2$O$_5$	440.8	20.3	3.74	1.648	0.304	7.6	1.40
(8) NiMoO$_4$–0.31TeO$_2$	441.2	21.5	3.60	1.627	0.273	9.6	1.61
(9) Te$_2$MoO$_7$	440.0	–	–	0.009	0.003	–	–
(10) Te$_2$MoO$_7$	533.0	–	–	0.543	0.157	12.0	3.47
(11) NiMoO$_4$—0.038Te$_2$MoO$_7$	440.0	17.2	2.54	1.825	0.269	5.4	0.80
(12) NiMoO$_4$–0.5MoO$_3$–0.013Te$_2$MoO$_7$	440.2	20.5	3.80	1.664	0.309	7.1	1.32
(13) NiMoO$_4$–MoO$_3$–0.018Te$_2$MoO$_7$	441.0	16.0	3.71	1.064	0.247	6.0	1.39
(14) NiO	441.0	18.2	0.85	5.461	0.255	8.7	0.41
(15) TeO$_2$	440.0	–	–	0.008	0.003	–	–
(16) TeO$_2$	545.0	80.0	7.98[***]	2.705	0.270	28.1	2.80[***]
(17) MoO$_3$	440.0	–	–	0.001	0.000	–	–
(18) MoO$_3$	545.7	13.0	1.17	0.318	0.029	2.8	0.25
(19) MoO$_2$[**]	441.5	–	–	0.001	0.000	–	–
(20) MoO$_2$[**]	546.0	15.7	1.26	0.381	0.030	4.1	0.33

[*]was prepared by heating α-NiMoO$_4$ up to 700°C then cooled to working temperature; [**]obtained in situ by reducing MoO$_3$; [***]hypothetical values including Te volatilisation
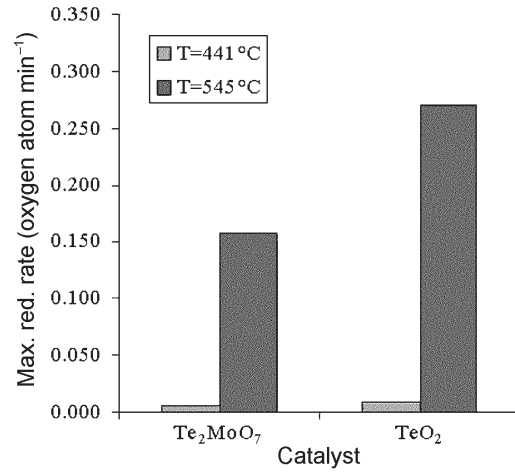
Fig. 2 Temperature effect on tellurium oxide and tellurium molybdate reduction
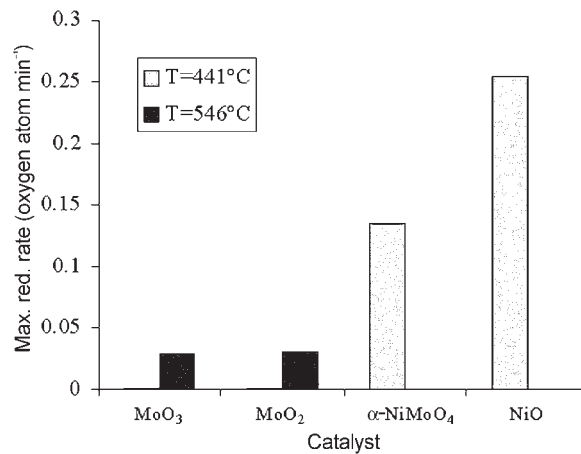

Fig. 3 Temperature effect on nickel–molybdenum oxides reduction

NiMoO₄ structure effect

In Fig. 4 the mass loss under hydrogen at 441°C for α- and β-NiMoO₄ is reported. It can be seen that the β phase has the greatest reduction rate. Table 1 reports the maximum reduction rate both on global % mass loss and on oxygen atoms loss base. The increase of oxygen lability is more important if it is evaluated on the basis of oxygen atoms lost per minute.
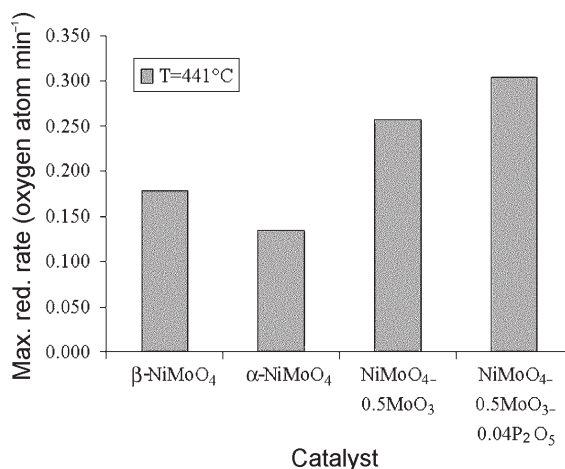
Fig. 4 Effect of the nature of the phase and of phosphorus oxide doping on nickel molybdate reduction

Under stoichiometric $Ni_{0.9}MoO_{3.9}$ system (Ni/Mo<1)

The reduction of the solid under the same conditions cited above have shown that the depletion rate was found to be of 1.053% min^{-1} i.e. 0.139 oxygen atoms min^{-1}. This reduction rate seems to be slightly higher with respect to the rate observed using a stoichiometric compound (0.984% min^{-1} i.e. 0.134 oxygen atoms min^{-1}). This result indicates that if the stoichiometric $NiMoO_4$ network is slightly modified the depletion rate of the lattice oxygen is almost constant although the electrical conductivity changes using understoichiometric instead of stoichiometric $NiMoO_4$ system [8].

MoO_3 dopant effect

The results reported in Table 1 and Fig. 5 indicate that, at a fixed temperature, increasing the molybdenum content (e.g., compare the runs performed with catalysts 4, 5 and 6), the reduction rate (mass%) of the solid drastically decreases in the order $NiMoO_4$–$0.5MoO_3$>$NiMoO_4$–MoO_3>$NiMoO_4$–$5MoO_3$ while in the case of understoichiometric nickel molybdate $Ni_{0.9}MoO_{3.9}$ (Ni/Mo<1) the reduction rate is slightly different with respect to the stoichiometric $NiMoO_4$ system. Furthermore, a noticeable increase of depletion rate is observed when the MoO_3 amount added is inferior or equal to 0.5 (catalyst 1 *vs.* catalysts 3 and 4). The effect is still marked when the reduction rate is expressed in terms of oxygen atoms loss per minute. These results indicate that the presence of MoO_3, specifically when the excess is larger than 0.5, decreases the oxygen extraction from the solid. When MoO_3 load is limited, the global reduction rate increases while when the MoO_3 concentration is high, the reduction rate tends to decrease rapidly probably due in part to the $NiMoO_4$ surface coverage limiting thus the access of hydrogen to the $NiMoO_4$ lattice oxygen. While the pure MoO_3 (catalyst 17) reduction was found to be negligible under the same operating
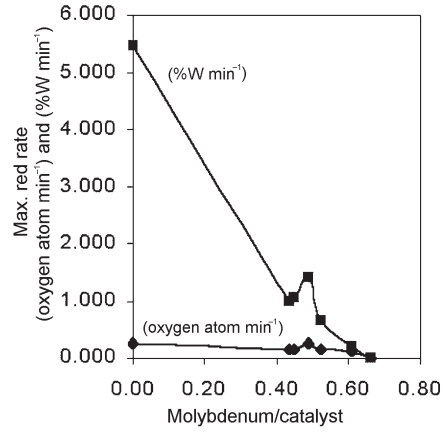
Fig. 5 Molybdenum load effect on $NiMoO_4$ oxygen depletion rate at 440°C

conditions (Table 1), $0.5MoO_3$–$NiMoO_4$ has been found to be the optimal composition (Mo/cat=0.5 mass/mass) leading to the highest reduction rate (Fig. 5).

The addition of P_2O_5, which has acid properties but has no oxidising power, affects positively the global reduction rate of the catalyst $NiMoO_4$–$0.5MoO_3$–P_2O_5 (1.648 *vs.* 1.420 % min^{-1} and 0.304 *vs.* 0.258 oxygen atoms min^{-1}) (Fig. 3 and Table 1).
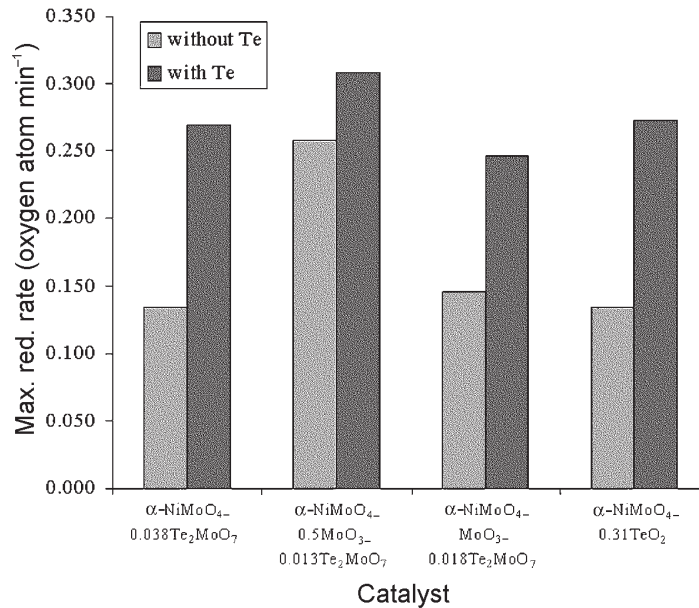

Fig. 6 Tellurium molybdate and tellurium oxide effects on Ni–Mo–O reduction rate

Effect of TeO$_2$ on NiMoO$_4$ reduction behaviour

Referring to the data reported in Table 1, it may be seen that promoting the stoichiometric NiMoO$_4$ by tellurium oxide drastically increases the reduction rate of the catalyst. The effect is much marked if the depletion rate is expressed in oxygen atoms lost per minute, a twofold increase is observed (Fig. 6).

It should also be noticed that, under the same reducing conditions of temperature and hydrogen flow rate, when tellurium oxide is engaged in a structure such as in Te$_2$MoO$_7$ its reduction rate is drastically decreased relative to the pure oxide TeO$_2$ (Fig. 2).

Effect of Te$_2$MoO$_7$ promoter on NiMoO$_4$ reduction behaviour

Under isothermal conditions (T=440°C) Te$_2$MoO$_7$ reduction observed was minimum (Fig. 2) while for the mixed molybdates NiMoO$_4$–Te$_2$MoO$_7$ the reduction rate has been found to be favoured (Fig. 6). Comparing the depletion rate obtained with the catalyst 1 or 9 reported in Table 1 with respect to the reduction rate of the catalyst formed by combining these two materials (catalyst 11) better results in terms of oxygen mobility were observed (0.134 *vs.* 0.269 oxygen atoms lost min^{-1}). These results show that although Te$_2$MoO$_7$ is slightly reducible under the operating conditions adopted, its interaction with NiMoO$_4$ generates a synergetic effect which leads to a higher reduction rate of the solid (mixed oxides) relative to the corresponding NiMoO$_4$ or Te$_2$MoO$_7$.

NiMoO$_4$–Te$_2$MoO$_7$ vs. NiMoO$_4$–xMoO$_3$ catalysts

The comparison of NiMoO$_4$–Te$_2$MoO$_7$ catalysts reduction behaviours relative to the NiMoO$_4$–xMoO$_3$–Te$_2$MoO$_7$ (0<x<1) working under hydrogen is shown in Table 1. Using NiMoO$_4$–Te$_2$MoO$_7$ systems in the presence of hydrogen, and at temperatures of 440°C the introduction of MoO$_3$ (0.5 to 1.0) induces a decrease of the reduction rate of the solid (mass% min^{-1}). This effect has also been observed reducing xMoO$_3$–NiMoO$_4$ systems (1<x<5) (Fig. 5) confirming the slow down reduction effect of the MoO$_3$.

Referring to the catalyst 0.5MoO$_3$–NiMoO$_4$ or MoO$_3$–NiMoO$_4$ their promotion with Te$_2$MoO$_7$ has been found to accelerate (Table 1 and Fig. 4 *vs.* Fig. 6) the respective reduction rate (catalysts 4 *vs.* 12 and 5 *vs.* 13). This reduction behaviour is favoured as mentioned above in the case of NiMoO$_4$ doped by Te$_2$MoO$_7$ systems (catalyst 1 *vs.* 11) . These observations lead to the conclusion that a similar reduction pathway must be involved.

Catalytic activity

Propane oxidative dehydrogenation (ODH) undoped and P- and/or Mo-, doped stoichiometric NiMoO$_4$ catalysts

The stoichiometric α- and β-NiMoO$_4$ and MoO$_3$ or/and P$_2$O$_5$ doped α-NiMoO$_4$ systems have been tested in the oxidative dehydrogenation of propane. Table 2 shows the catalytic activity measured in the range of temperatures of 500 and 530°C.

It can be noticed that, at all the temperatures studied, while the highest propane conversion is obtained with $0.5MoO_3$–P_2O_5 doped α-$NiMoO_4$, propylene selectivity is better with pure β-$NiMoO_4$. These results indicate that the former is more active but less selective than β phase. When the results are expressed in terms of intrinsic propane conversion or intrinsic propylene selectivity the β phase is better as its active surface area is lower (10.5 m^2 g^{-1}) compared to the surface area of the α phase (41.9 m^2 g^{-1}) and (21.4 m^2 g^{-1} for $0.5MoO_3$–P_2O_5). The same conclusions can be drawn regarding propylene yield (mmol h^{-1} m^{-2} or mmol h^{-1} m^{-2} g_{cat}^{-1}).

Finally, a comparison in terms of propylene yield (C_3H_6 mmol $g_{NiMoO_4}^{-1}$) shows that the β phase is sensibly better. The differences observed were mainly due to a drop of CO_x selectivity, which could be attributed to the oxygen molybdenum co-ordination (i.e. structure). In fact, an increase in catalytic performance passing from α to β-phase corresponds to a higher H_2 reduction rate in TG tests i.e a higher lattice oxygen-consuming rate of the β-$NiMoO_4$ relative to the α-phase (Table 1). The trend is also confirmed at higher temperatures up to 560°C above which β phase starts to form with time [9]. This correlation and the observed relationship between the catalyst activity, in continuous flow reactor (this work) or more specifically in periodic flow reactor [10], and reducibility confirms that the lattice oxygen plays a crucial role in oxidative dehydrogenation of propane. Referring to the apparent activation energy, data obtained for the solid reduction (46–50.2 kJ $kmol^{-1}$) compared with those obtained for propane oxydehydrogenation (54.3–62.7 kJ $kmol^{-1}$) using only lattice oxygen [11] have been found to be quite close. These results taken together provides a strong evidence for the suggestion that the reaction is governed by a red-ox mechanism [12].

When dealing with oxides like activate oxygen, two aspects must be taken into account: a) the quantity of adsorbed oxygen and b) the oxygen exchange rate. Data reported in literature on $NiMoO_4$ indicate very low values both for oxygen adsorption [13] and exchange rate [14]. These two characteristics, according to Bielanski and Haber [13], explain the good selectivity obtained in the oxidative dehydrogenation reaction. Referring to β-$NiMoO_4$ phase (catalyst 2 in Table 1) the oxygen (atom/formula) lost, between the initial time of reduction until the time at which the reduction rate reach its maximum (last column of Table 1), is lower with respect to the oxygen lost for α phase. This indicate that small amounts of oxygen of the solid can be extracted and restored in a minor time for β phase with respect to α phase. This could explain a better red-ox cycle during catalytic tests for the former phase.

Referring to propane ODH results obtained in the presence of $0.5MoO_3$–$NiMoO_4$ or $0.5MoO_3$–$NiMoO_4$–P_2O_5 (Table 2) it can be observed, by comparing pure α-$NiMoO_4$ activity with MoO_3 or MoO_3–P_2O_5 doped stoichiometric system, an increase of propane conversion accompanied by a noticeable increase in propylene selectivity [15] and particularly for $0.5MoO_3$–P_2O_5–$NiMoO_4$. If the results are expressed in terms of propylene yield the latter system is better. The improvement of catalytic performances using the cited combined oxides can be explained, on the one hand, in terms of a synergetic effect and, on the other hand, by MoO_3, which plays an

Table 2 Oxidative dehydrogenation of propane into propylene on undoped and MoO_3 and or P_2O_5 $NiMoO_4$ systems

| Catalysts | $T/°C$ | Conv/% | Selectivity/% | | | | | | C_3H_6 yield | |
			CO	CO_2	C_2H_4	C_3H_6	C_2H_{4O}	C_3H_{4O}	mmol h^{-1} m^{-2}	mmol h^{-1} g$_{cat}^{-1}$
α-NiMoO$_4$	500	9.6	23.0	21.4	2.0	49.0	0.6	4.0	0.22	9.4
α-NiMoO$_4$	530	15.2	27.0	21.0	2.0	46.2	0.8	3.0	0.33	14.0
β-NiMoO$_4$	500	7.2	10.3	8.0	0.7	78.1	0.3	2.6	1.06	11.2
β-NiMoO$_4$	530	12.5	12.0	10.1	1.0	73.0	0.9	3.0	1.73	18.2
0.5MoO$_3$/α-NiMoO$_4$	530	20.1	35.3	13.9	0.0	45.3	0.0	5.5	0.40	9.1
0.5MoO$_3$–P$_2$O$_5$/α-NiMoO$_4$	530	22.3	20.8	16.3	0.4	59.4	0.0	3.1	0.62	13.2

15% C_3H_8, 15% O_2 in N_2, total feed 15l/h, for 500 mg catalyst

'oxygen reservoir' role for $NiMoO_4$ according to a remote control mechanism [16–19]. Thus the irreversible deep reduction on stream of pure $NiMoO_4$ phase to NiO and MoO_2 is inhibited when MoO_3 is present. The catalytic behaviour of metal molybdates being generally attributed to the presence of molybdenum reduced species such as Mo^{5+} [20] generated by hydrocarbons or hydrogen surface reduction (monolayer) [10].

Table 3 effect of MoO_3 on propylene activation

Catalysts	$T/°C$	Conv/ %	Selectivity /%				
			C_3H_4O	$C_3H_4O_2$	CO_x	C_2H_4O	$C_2H_4O_2$
α-$NiMoO_4$	420	10.5	5.1	1.0	91.1	0.8	2.0
$0.5MoO_3/\alpha$-$NiMoO_4$	420	14.2	6.1	3.5	85.0	1.4	4.0
MoO_3/α-$NiMoO_4$	420	17.6	13.0	30.0	47.0	2.7	7.3
$5MoO_3/\alpha$-$NiMoO_4$	440	9.4	30.0	22.2	41.1	2.2	4.5
$12MoO_3/\alpha$-$NiMoO_4$	450	2.6	47.3	8.7	38.1	1.8	4.1
MoO_3	420	0.3	60.6	0.8	33.3	1.5	3.8

$C_3H_6/O_2/N_2$=10/10/80, contact time 0.1 g h L^{-1}

Table 4 Propylene conversion and products selectivity on Te– and Mo–doped $NiMoO_4$ system

Catalysts	$\tau/$ g h L^{-1}	Conv/ %	Selectivity/%				
			C_3H_4O	$C_3H_4O_2$	CO_x	C_2H_4O	$C_2H_4O_2$
α-$NiMoO_4$	0.1	10.5	5.1	1.0	91.1	0.8	2.0
Te_2MoO_7	0.1	1.7	76.7	8.7	11.2	1.2	4.0
MoO_3/α-$NiMoO_4$	0.1	17.6	14.7	30.0	47.0	1.0	7.3
MoO_3–Te_2MoO_7/α-$NiMoO_4$	0.1	78.3	53.0	27.0	18.6	0.6	0.8
MoO_3–Te_2MoO_7/α-$NiMoO_4$	0.3	97.0	28.4	46.3	24.5	0.2	0.6
MoO_3–Te_2MoO_7/α-$NiMoO_4$ +10% H_2O vapour	0.3	96.0	12.8	59.1	23.8	0.3	4.0

$C_3H_6/O_2/N_2$=10/10/80, T= 420°C, τ=contact time

Propylene partial oxidation (PO)

Propylene partial oxidation is performed using binary or ternary systems such as MoO_3–$NiMoO_4$ and MoO_3–Te_2MoO_7–$NiMoO_4$ and the catalytic data are reported in Tables 3 and 4.

Effect of MoO_3

The effect of MoO_3 on the catalytic activity in propylene oxidation reaction was studied. The catalytic results obtained with MoO_3 doped–$NiMoO_4$ systems are reported in Table 3. It can be observed when a small load of MoO_3 ($MoO_3/NiMoO_4 \leq 1$) is present together with stoichiometric α-$NiMoO_4$ catalyst, in which MoO_3 is distributed homo-

geneously due to the preparation method adopted [6], the propylene conversion is increased and the carbon oxides formation is decreased leading to a significant increase of the selectivity in acrolein and acrylic acid. On the contrary, if MoO_3 contents are high, the propylene conversion decreases even at higher temperatures while a good selectivity towards oxygenates is maintained. Finally, if MoO_3 is used alone, the propylene conversion is negligible and only traces of acrylic acid are present.

Referring now to the isothermal reduction behaviour at 440°C of the same oxides under hydrogen, it can be observed that a higher production of carbon oxides corresponds to a higher reduction rate of the solids. It should also be noticed that although the depletion rate is slowed down increasing the MoO_3 concentration, the total oxygen available at the maximum reduction rate increases (Table 1). The comparison of the six systems (Table 3) shows that both propylene conversion and acrolein and acrylic acid selectivities obtained with $MoO_3/NiMoO_4$ are better using Mo/Ni of 2/1 instead of 1.5/1 or 1/1 ratio and lower temperatures. Similar beneficial effects by a small amount of Mo and W doping over catalysts were found by Popova *et al.* [21, 22]. When MoO_3 content is drastically increased (Mo/Ni=13/1 or MoO_3 alone) the formation of acrolein and acrylic acid is favoured to the detriment of propylene conversion even at higher temperatures. This fact can be explained in terms of a molecular oxygen activation on the catalytic surface rather than a catalyst lattice oxygen participation which is in agreement with the reduction rate of the corresponding oxides (Table 1).

Effect of Te_2MoO_7

Runs performed with tellurium containing catalysts in the propylene partial oxidation are reported in Table 4. Relative to $NiMoO_4$ the Te_2MoO_7 catalyst shows a low conversion with a high acrolein selectivity. The activity of Te_2MoO_7 can be attributed to both the low depletion rate and to the low specific surface area (Table 1, Fig. 2). Under the same operating conditions the binary system $NiMoO_4$–MoO_3 has been found to be more active and selective towards C_3H_4O and $C_3H_4O_2$ with respect to the separate oxides $NiMoO_4$ and MoO_3 (Table 3), while the introduction of Te_2MoO_7 in the $NiMoO_4$–MoO_3 (Table 4) system has shown a subsequent increase of the catalytic performances either in terms of propylene conversion (78.3 *vs.* 17.6%) or in selectivity to acrolein (53 *vs.* 14.7%).

In dealing with the partial oxidation of C_3H_6 the competitive combustion of propylene and the degradation of the oxygenated products is known to be greatly limited by Te–Mo based catalysts in the presence of water vapour. Tests performed with $NiMoO_4$–MoO_3–Te_2MoO_7 system in the presence of water vapour lead to a subsequent increase of the conversion and more specifically shift the equilibrium towards the formation of acrylic acid due to conversion of the acrolein formed. All these observations are in agreement with the reduction tests performed under hydrogen. In the range of temperatures investigated the mixture of $NiMoO_4$, a solid moderately reducible, together with MoO_3 and Te_2MoO_7, both slightly reducible, leads to the formation

of a catalyst more reducible due to a synergetic effect generated by these phases (Table 1 and Fig. 6).

A preliminary kinetic study has been performed with MoO_3–Te_2MoO_7–α-$NiMoO_4$ in order to discriminate between the rate of formation of acrolein and acrylic acid. It has been found that the rate of acrolein formation is slower. Accordingly we have extended the kinetic study by using a power-law expression of the form $r = k_0 e^{-E_a/RT} P_{O_2}^m P_{C_3H_6}^n$. The experimental data have shown that the reaction order m with respect to oxygen is 0.39; 0.23 and 0.48 respectively for CO, CO_2 and acrolein formation. The corresponding order n with respect to propylene was 0.43; 0.49 and 0.32. Thus, it may be stated that the observed kinetic values do not justify a conventional red-ox mechanism and that the yield of acrolein can be improved by lowering propylene and by increasing oxygen partial pressures.
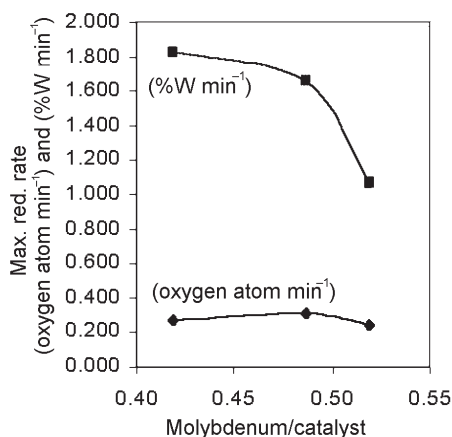

Fig. 7 Molybdenum load effect on oxygen depletion rate of tellurium oxide containing catalysts at 440°C

With Te–doped–$NiMoO_4$ catalysts both in the presence and in the absence of the water vapour, acrolein was always present together with carbon oxides. These observations lead to the conclusion that an allylic reaction intermediate must be involved (Fig. 8). The rate of allylic oxidation is controlled by the rate of allylic-intermediate formation and the presence of TeO_2 favours the formation of allylic oxidation products (especially acrolein) at the expenses of hydration products [23]. Taking into consideration their ability to give high propylene conversion as well as considerable se-
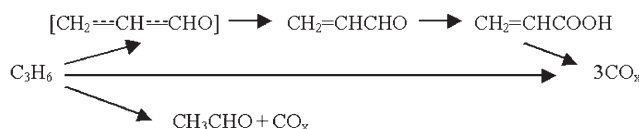

Fig. 8 Reaction pathway for propylene oxidation with Ni–Mo–O systems

lectivity to acrolein and acrylic acid, Te doped–Ni–Mo–O catalysts can be considered to have a potential for propylene partial oxidation linked also to the increase of the catalyst reducibility induced by the presence of tellurium doping element although the reaction is governed by the molecular oxygen partial pressure rather than lattice oxygen.

Conclusions

The mobility of polymorphic $NiMoO_4$ lattice oxygen has been studied by isothermal reduction under hydrogen at different temperatures where the oxygen depletion rate has been evidenced to be dependent on $NiMoO_4$ phases.

The presence of MoO_3, TeO_2, Te_2MoO_7 and P_2O_5 promoters affect simultaneously the reduction rate and lattice oxygen mobility of Ni–Mo–O catalysts.

Lattice oxygen mobility of undoped and doped $NiMoO_4$ materials has also been investigated by propane oxydehydrogenation (ODH) and propylene oxidation (PO) performed either with a continuous and periodic flow micro-reactors.

While ODH over Ni–Mo–O systems was found to be related to the reducibility of the catalysts i.e. to corresponding Mo and Ni oxygen co-ordinations in the stoichiometric α- and β-$NiMoO_4$ systems, the PO carried out with Ni–Mo–Te–O ternary catalysts is governed both by molecular partial pressure and by the synergetic effect generated by combining $NiMoO_4$ with MoO_3, TeO_2 and/or Te_2MoO_7.

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