Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 267–277

ISOTHERMAL REDUCTION BEHAVIOUR OF UNDOPED AND Ca-, K- AND P-DOPED $NiMoO_4$ PHASES USED FOR SELECTIVE PROPANE OXYDEHYDROGENATION

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(Received September 18, 2000)

Abstract

Isothermal reduction under hydrogen of polymorphic $NiMoO_4$ system has been studied at different temperatures using thermogravimetry. Evidences found by TG (oxygen depletion rate) have shown a dependence on lattice oxygen mobility and source due to the crystal structure and temperature.

Relative to the undoped $NiMoO_4$ phases, it has been found that the presence of K_2O, CaO and P_2O_5 promoters simultaneously affects both the reduction rate and the oxygen source.

Monolayer lattice oxygen mobility of undoped and doped $NiMoO_4$ material was investigated by oxydehydrogenation of light alkanes performed by using a periodic flow micro-reactor. The alkane activity has been found to be linked to the reduction behaviour of the different undoped and doped $NiMoO_4$ phases.

Keywords: isothermal reduction, lattice oxygen, polymorphic nickel molybdate, *red-ox* properties

Introduction

Inorganic metal-oxygen materials are of great interest in heterogeneous catalysis and ceramic chemistry. One important aspect of the chemistry of these compounds is their thermal behaviour, lattice oxygen mobility and structure defects [1, 2].

In previous works, unpromoted and promoted molybdate catalysts were prepared by different techniques [3–5] but, to our knowledge, experimental data are lacking on isothermal reduction of α and β phases of stoichiometric $NiMoO_4$ doped catalysts. The $NiMoO_4$ compound is interesting as active catalyst for the oxidation of light alkanes to their corresponding alkenes [6, 7]. In more recent works, we verified and completed the study of the behaviour of all $NiMoO_4$ phases working in a *red-ox* cyclic mode [8, 9].

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1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Hereafter, we report the observed oxygen depletion rate during isothermal reduction under hydrogen of all undoped and K_2O–, CaO– and P_2O_5–$NiMoO_4$ phases. The structural, superficial acid-base properties and activity of each phase are compared.

Experimental

$NiMoO_4$ preparation

A Mettler RC1 Reaction Calorimeter was used allowing a careful control of the main experimental parameters (T, stirring speed, pH, etc.) which determine the structure and surface characteristics of the active catalyst [3]. The stoichiometric catalyst $NiMoO_4$ was prepared by co-precipitation from an equimolar molybdic acid and nickel nitrate solution (0.25 mol l^{-1}), at 85°C with the pH adjusted at 5.25 by addition of ammonia. The resulting precipitate was hot filtered, dried at 120°C for 15 h and then heated at 550°C for 2 h leading to α-$NiMoO_4$ formation. The β-$NiMoO_4$ phase was obtained *in situ* by thermal treatment of the α-phase up to 720°C which was then cooled to reaction temperatures. The α'-phase is obtained by heating beyond 720°C and complete cooling to ambient temperature. The catalyst particle size was found to be in the range of 200–325 mesh.

Promoted catalysts

Incipient wetness impregnation technique was used to prepare K_2O, CaO and P_2O_5 promoted $NiMoO_4$ catalysts. The impregnation was made to start from stoichiometric $NiMoO_4$ activated (at T=550°C) catalyst and KOH, $Ca(NO_3)_2$, and $(NH_4)_2HPO_4$ salts. A further treatment at 550°C for two hours allowed to obtain the final catalyst. The dopant percentages indicate the mass of the doping element with respect to the total mass of the catalyst.

Thermal studies of the compounds were carried out on a Seiko TG-DTA instrument. Weighed samples (*ca.* 20 mg) were placed in alumina crucibles and reduction tests were carried out isothermally under a hydrogen atmosphere (gas feed 3 l h^{-1}) while recording the TG and DTG curves. For α- and α'-phases the samples were preheated (10°C min^{-1}) in air up to the reduction temperature (T_r) and were then washed (20 min) with helium. For β-phase the sample was heated (10°C min^{-1}) up to 720°C and cooled (10°C min^{-1}) to the reduction temperature (T_r) under air and was then washed (20 min) with helium prior to the introduction of hydrogen.

Results and discussion

The difficulty of removing oxygen from the lattice of a solid is often related to the strength of the metal-oxygen bond. The weaker the bond is, the higher the lattice oxygen mobility is and vice versa. However, in selective oxidation reactions, it is generally observed that the activity and selectivity of an oxide are related to its reducibility.

High resistance to reducibility leads to a lower activity, while easier reducibility implies a higher activity but also a lower selectivity.

At atmospheric pressure the system studied, stoichiometric nickel molybdate presents two polymorphic phases: the low-temperature α-phase, with molybdenum in a distorted octahedral environment [10, 11], and the high-temperature β-phase, with molybdenum in a distorted tetrahedral site [12]. The β-phase is formed after heating the α-phase up to 720°C and undergoes reverse transition at low temperature on cooling at *ca.* 200°C. The complete cooling to ambient temperature leads to the formation of the α'-$NiMoO_4$ phase which possesses the same structure of the α-phase, with molybdenum in a distorted octahedral environment. The α'-phase differs only in its specific surface area which is lower (13 *vs.* 33 $m^2 g^{-1}$ for the α-phase) due to the thermal treatment at high temperature (720 *vs.* 550°C). The $\alpha \rightarrow \beta$ transition occurs without mass loss. A progressive MoO_3 sublimation from $NiMoO_4$ may be observed at temperature higher than 720°C. In Fig. 1 the DTA cycle of phase transitions of the stoichiometric $NiMoO_4$ system is shown.

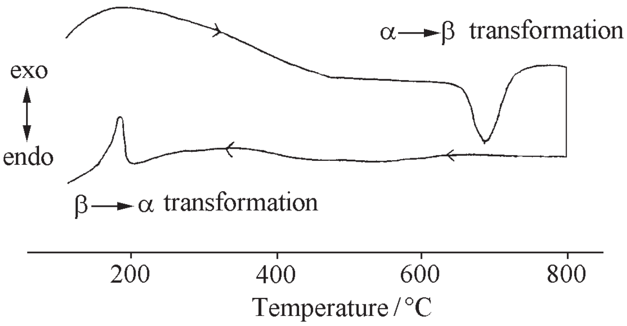

Fig. 1 DTA cycle of stoichiometric $NiMoO_4$ phase transitions

The isothermal reduction of $NiMoO_4$ based systems was performed under hydrogen at different temperatures. In Fig. 2 the effect of temperature on reduction behaviour of pure α, β and α'-$NiMoO_4$ phases with a constant H_2 concentration is shown.

Noticeable differences in terms of reduction rate *vs.* temperature for each phase can be evidenced. These variations are due to the increase of oxygen mobility with temperature. A comparison of the reduction trends of the three phases, for example at 460°C (Fig. 3), shows that the depletion rate evolve in the following order β-$NiMoO_4$>α'-$NiMoO_4$>α-$NiMoO_4$. These behaviours may be attributed to the weaker strength of M–O bonds in the corresponding structures.

Regarding the general reduction trend, it can be seen that $NiMoO_4$ presents two steps of reduction with different slopes which indicate a consecutive depletion of different types of oxygen. In order to better investigate the observed behaviours we have reported in Fig. 4 the DTG *vs.* TG curves profile of the pure phases *i.e.* the reduction rate *vs.* reduction degree.

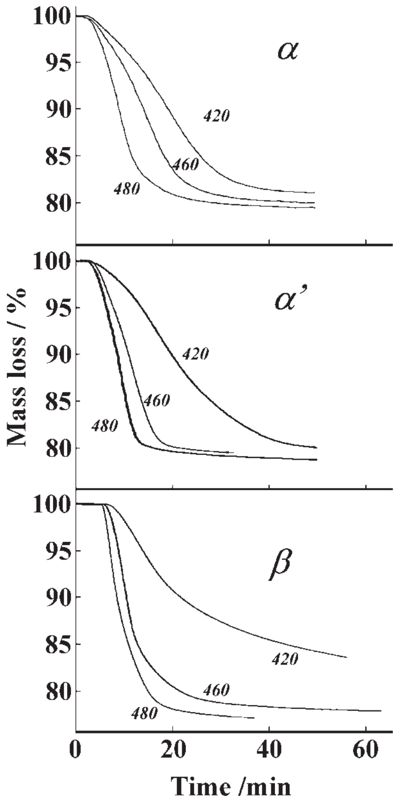

Fig. 2 Effect of temperature on reduction behaviour of $NiMoO_4$

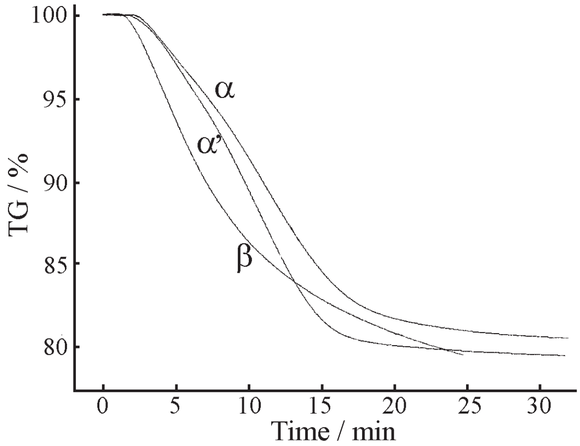

Fig. 3 TG mass loss *vs*. time for α-, α'- and β-$NiMoO_4$ under hydrogen at 420°C

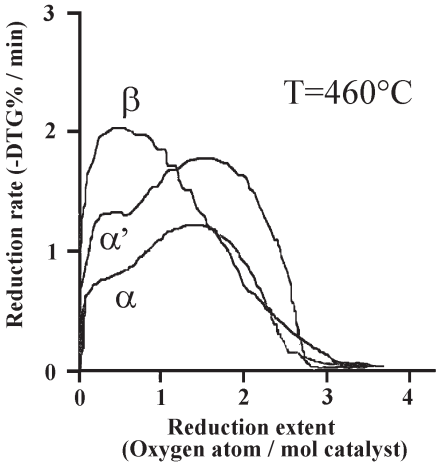

Fig. 4 Reduction rate *vs.* reduction extent (*i.e.* DTG *vs.* TG curves) of $NiMoO_4$ pure phases at 460°C

These results lead to hypothesise that in all cases there are at least two oxygen types which could be extracted consecutively during reduction. These two oxygen bonds could be attributed to Ni–O and Mo–O metal oxides present in the structure of $NiMoO_4$ since the oxygen coordination of the two metals is different. Nickel is surrounded by four oxygen atoms in a tetrahedral symmetry while Molybdenum coordination is six in an octahedral symmetry.

In the case of the β-phase where both nickel and molybdenum are in a tetrahedral symmetry, these two peaks are partially overlapped and inverted.

The products composition obtained from α-$NiMoO_4$ reduction have not been established unambiguously. In the literature some mechanisms are proposed for the reduction of the Ni–Mo–O system, but the intermediates as well as the final products of reduction differ from author to author [13–17]. In order to obtain a deeper understanding of our systems, a study of both $NiMoO_4$ phases reduction was performed with the main objective of identifying the reduction products. In this sense, XRD analyses were performed after isothermal reduction runs at selected temperatures 420–480°C. The XRD spectra showed the presence of three broad peaks characteristic of metallic nickel and/or of the intermetallic Ni_4Mo (JCPDS cards 4–850 and 3–1036, respectively). The formation of the intermetallic Ni_4Mo (d=2.052Å) was also reported by Brito *et al.* [13], whereas other authors [14] reported that such a compound can be a reduction product of anhydrous nickel molybdate.

A deep reduction performed at higher temperatures leads to peaks characteristic of MoO_2 (JCPDS card 5-452). This phase was reported in almost all work regarding $NiMoO_4$ reduction, however, some authors found amorphous material. Kipnis *et al.* [15] proposed that the reduction of α-nickel molybdate by hydrogen at 400–500°C leads to the formation of a Ni–Mo alloy and a finely dispersed lower Mo oxide phase that crystallises as MoO_2 when heated at 600°C. According to Brito *et al.* [13] reduction of MoO_3 to MoO_2 under dynamic conditions of TPR proceeds with the formation of highly amorphous oxide. These facts explain the broadness of the peaks in the X-ray diffractograms and the absence of the MoO_2 characteristic lines.

Since the molybdenum in α-$NiMoO_4$ and MoO_2 is in an octahedral co-ordination, it is most probable that the MoO_2 phase formed by low temperature reduction of α-$NiMoO_4$ is built up of MoO_6 octahedra connected irregularly by both vertices and edges. On the other hand, it is known that the formation of a solid solution of molybdenum in nickel leads to an increase in the lattice constants, manifested in a shift of the nickel lines on the X-rays diffractogram towards smaller angles. On the basis of our data, when the α-$NiMoO_4$ is subjected to reduction (H_2) and heating ($420<T<480$°C), the following reduction scheme can be proposed: $NiMoO_4 \rightarrow Ni+Ni_4Mo+$ amorphous MoO_2. At temperatures lower than 500°C the reduction of α-$NiMoO_4$ has led to the formation of an unordered nickel–molybdenum alloy with a concentration dishomogeneity in the distribution of Mo and Ni. Referring to the β-$NiMoO_4$ phase, the observed reduction behaviour was found to be different from the α-$NiMoO_4$ one; both reduction trend and rate are different (Figs 2 and 4). The reduction scheme reported above may be still valid for the β-phase but with a different reduction products concentration.

In the light of these findings and in order to get a deeper understanding of the depletion mechanism of $NiMoO_4$ system, different basic promoters, such as CaO and K_2O (usually used for alkanes oxydehydrogenation reaction) were introduced in $NiMoO_4$ systems by impregnation technique. After calcination of the impregnated samples at 550°C, the effect of these doping element on the depletion rate was studied by TG-DTG analyses. As an example, CaO and K_2O doped α-$NiMoO_4$ systems are reported in Fig. 5.

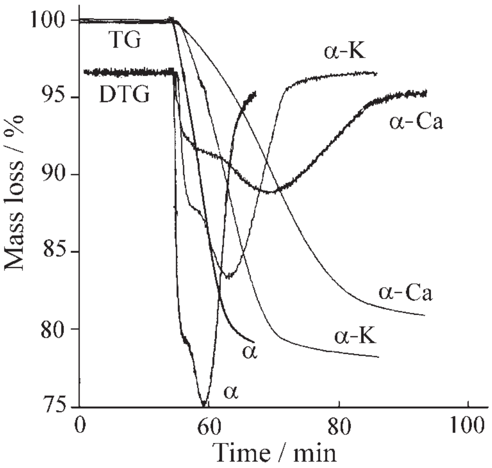

Fig. 5 TG-DTG of undoped and CaO or K_2O doped α-$NiMoO_4$ system

It can be noticed that, following the addition of the promoters, the reduction rate decreases indicating that the mobility of the oxygen has become less important. With respect to the easier oxygen depletion rate of $NiMoO_4$ pure phases, the reduction rate is restrained by the introduction of basic promoters.

In the case of calcium doped catalyst a higher percent (ca. 10 fold increase) of the dopant was necessary to obtain the same basicity as that of K_2O doped catalysts [9]. It should also be observed that although the basicity is the same, the reduction rates of $NiMoO_4$/0.1% K and α-$NiMoO_4$/1% Ca are different. CaO load has a more significant effect on the reduction rate than K_2O load.

In order to obtain a better understanding of the relationship between acid-base properties and reducibilty of the catalysts, it was decided to introduce a second acidic promoter, P_2O_5, which is often used in ODH reaction for increasing alkanes conversion to counterbalance the effect of the cited basic promoters. The reduction behaviour of the Ca–P/α-$NiMoO_4$ and K–P/α-$NiMoO_4$ prepared systems was studied. If compared to the CaO and K_2O-doped catalysts, the reduction profile of Ca–P/α-$NiMoO_4$ and K–P/α-$NiMoO_4$ showed that the depletion rate was subsequently lowered in presence of P_2O_5 (Fig. 6).

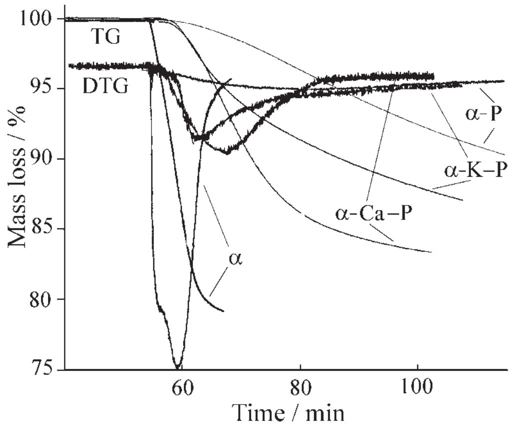

Fig. 6 TG-DTG of undoped and P, Ca–P and K–P doped α-$NiMoO_4$ system

Referring to the reduction rate *vs.* reduction degree curves (Figs 4–6), it is also important to notice that while no significant change was observed in the general trend of DTG *vs.* TG curves when the pure phases were doped with Ca or K (Fig. 5), the addition of phosphorus on pure phases (P/α-$NiMoO_4$) and on doped $NiMoO_4$ (Ca–P/α-$NiMoO_4$ and K–P/α-$NiMoO_4$) leads to an inhibition of the second peak formation (Fig. 6). This is probably due to a rearrangement of the oxygen network so that only one oxygen type is available for reduction. A possible explanation can be that a reaction between metallic nickel, formed during reduction, and phosphorus oxide occurs yielding a new crystalline phase $Ni_2P_2O_7$ (pyrochlore compounds) not detectable by XRD due the low amounts formed.

These results suggest that the introduction of P_2O_5 promoter decreases the reduction rate of the Ca/α-$NiMoO_4$ and K/α-$NiMoO_4$. This reduction rate does not reach the same level as for P_2O_5/α-$NiMoO_4$ catalyst as the promoters basicity (Ca and K) decreases the interaction between P_2O_5 and $NiMoO_4$. Consequently, the curves in Fig. 6 are shifted toward the P_2O_5/α-$NiMoO_4$ curve, but above those of Ca/α-$NiMoO_4$ and K/α-$NiMoO_4$ (Fig. 5). The same reduction experiments under hydrogen carried out with α-$NiMoO_4$/ 0.1% K, α-$NiMoO_4$/1% Ca, Ca–P/α-$NiMoO_4$ and K–P/α-$NiMoO_4$ were performed with the corresponding doped β-phase systems. The data obtained (not reported) showed that depletion rate was drastically lowered and in particular with Ca–P and K–P doped catalysts.

The catalytic effect of phosphorus was studied by preparing a catalyst where only P_2O_5 is present (P/$NiMoO_4$). The effects of the acidic promoter P_2O_5 on both the α→β phase transition under air, and the reducibility of the β-$NiMoO_4$ phase under hydrogen were studied by using the thermogravimetric technique.

Effect on the α→β phase transition

In the case of P/α-$NiMoO_4$ (i.e activated under air at $T\leq550°C$) the phosphorus maintains its initial structure P_2O_5 while if this system is treated in order to form the β-phase (i.e. activated under air at $T\geq720°C$) the phosphorus oxide would appear to be present in another crystalline form. The phosphorus oxide seems to accelerate the sublimation of the MoO_3 contained in the $NiMoO_4$ network (competition in terms of acidity between MoO_3 and P_2O_5). At ca. 590°C an abrupt mass loss of ca. 5% is recorded (Fig. 7). This mass loss was not observed for the undoped catalysts or for the catalysts doped with both phosphorus and CaO or K_2O. This fact can be explained in terms of the acid-base affinity between basic promoters (CaO or K_2O) and acidic phosphorus which could limit the interaction between phosphorus and $NiMoO_4$ at high temperature. The α→β transition occurs in both doped and undoped $NiMoO_4$ systems by a rearrangement of the oxygen co-ordination around the molybdenum. During the transition both Ni–O and Mo–O bonds in the network are weakened.

Effect on the reducibility of β-$NiMoO_4$

After cooling the P/β-$NiMoO_4$ (prepared activating P/α-$NiMoO_4$ under air at $T\geq720°C$) to the reduction temperature, tests carried out under hydrogen show that P_2O_5 in P/α-$NiMoO_4$ (Fig. 6) and P/β-$NiMoO_4$ (Fig. 7), lowers the depletion rate with respect to the undoped catalysts, particularly in the case of the β-phase as for the catalysts twice doped (Ca–P/$NiMoO_4$ and K–P/$NiMoO_4$).

These results evidence a strong interaction between the P_2O_5 and the $NiMoO_4$ system although the reduction of phosphorus to its metallic state is highly unlikely. The formation of a stable P–O–Mo and/or P–O–Ni surface compound during the initial catalyst reduction would account for these findings. This is also consistent with the observation that only relatively small additions of phosphorus to the CaO or K_2O doped catalysts are needed to produce the maximum effect on propene synthesis.

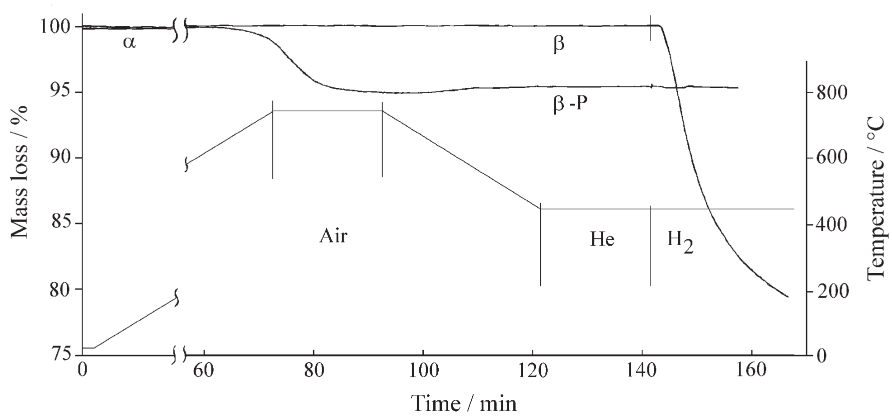

Fig. 7 Mass loss of $NiMoO_4$ and $P/NiMoO_4$, during α-β phase transformation under air and during reduction under hydrogen

Catalytic behaviour of the catalysts under propane atmosphere

Catalytic tests performed in a periodic-flow micro-reactor [8] have shown (Table 1) that although the presence of P_2O_5 did not increase the overall reduction rate of the catalysts (Ca–P and K–P doped $NiMoO_4$) the propane conversion is enhanced with respect to Ca and K doped catalysts. These observations can be supported by the fact that P_2O_5 is a typical acidic element (with no oxidising power) which induce an increase of the $NiMoO_4$ acidity leading to an increase of propane adsorption on the $NiMoO_4$ surface. As a consequence a higher propane conversion is obtained after reaction with monolayer oxygen of the catalyst. The possible contribution of the new $Ni_2P_2O_7$ phase formed could also be taken into account since in oxidative dehydrogenation of isobutane into isobutene higher yields are found [18, 19].

Table 1 Activity and selectivity of undoped and doped α and β-$NiMoO_4$

Catalyst *T*=500°C	Pulse period/s	Conversion/% C_3H_8	Selectivity/% C_3H_6	C_3H_6 yield (mmol $min^{-1}g_{cat}$)
α-$NiMoO_4$	40	3.70	74.62	0.074
α-$NiMoO_4$/0.1%K	40	1.61	89.35	0.038
α-$NiMoO_4$/0.1%K-2%P	40	3.73	84.50	0.084
α-$NiMoO_4$/1%Ca	40	2.64	81.15	0.058
α-$NiMoO_4$/1%Ca-2%P	40	3.77	76.42	0.080
β-$NiMoO_4$	40	1.70	94.40	0.042
β-$NiMoO_4$/0.1%K-2%P	40	2.78	94.01	0.070
β-$NiMoO_4$/1%Ca-2%P	40	2.85	87.86	0.066

Contact time : 0.3 g L^{-1} h^{-1} , helium washing gas feed : 3.6 L h^{-1}

Referring to the apparent activation energy the data obtained for the solid reduction compared with those obtained for propane oxydehydrogenation using only lattice oxygen (pulse reactor) are quite close and are in the range of 58.5–79.4 kJ mol^{-1}.

This interesting fact implies that some of M–O bonds are broken selectively and the surface oxygen vacancies created in the solid reduction step are related partly to the type of oxygen involved in the propane oxidation which can be removed and replaced during the reduction-oxidation steps.

As the catalytic results evidenced the longer the period (reduction degree) is, the best the alkene yield is; it is, therefore, possible to correlate the reduction behaviour of $NiMoO_4$ based system with the catalytic activity. It can also be noted that an elucidation of the structure of the amorphous molybdenum oxide phase together with a hypothetical presence of a newly formed $Ni_2P_2O_7$ phase can be of great interest, since their catalytic properties are important.

Conclusions

Source and 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 of the $NiMoO_4$ phases. The presence of K_2O, CaO and P_2O_5 promoters simultaneously affect the reduction rate and oxygen source. Monolayer lattice oxygen mobility of undoped and doped $NiMoO_4$ materials has also been investigated by propane oxydehydrogenation. The catalytic activity measured with a periodic flow micro-reactor was found to be related to the reducibility of the catalysts, which may be explained in terms of their corresponding Mo and Ni oxygen co-ordinations. The presence of P_2O_5, typical element, increases the surface acidity, decreases subsequently the overall reduction rate of the pure and doped catalysts (Ca–P and K–P doped $NiMoO_4$) and enhances the propane conversion.

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Financial support of CNR and of Polytechnic of Milano through ‘assegno di ricerca’ to A. Kaddouri is gratefully acknowledged.

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