

Selective propene formation in periodic flow reactor: reducibility and catalytic activity of Ni–Mo–O system

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Oxidative dehydrogenation (ODH) of propane with lattice oxygen of α -, α' - and β -NiMoO₄ phases has been studied. Reduction tests of the different phases were performed by TG analysis under hydrogen at different temperatures. Under isothermal conditions lattice-oxygen-consumption rate was found to be higher on the β -phase with respect to the α - and α' -phases. TG analyses showed the existence of different sources of lattice oxygen in the catalyst, depending on the NiMoO₄ phase. Catalytic activity was measured under steady state conditions, using a periodic flow reactor and it was then correlated to the reduction curve. It was found that the activation energy for ODH reaction over NiMoO₄ of 54.3–62.7 kJ/mol is nearly identical to that obtained for the catalyst reduction under hydrogen (46–50.2 kJ/mol). The correlation between the activation energy of the reaction in a periodic operating system (POS) and that of solid reduction under hydrogen suggests that the reaction obeys a red–ox mechanism.

Keywords: reducibility, NiMoO₄ lattice oxygen, propane ODH, apparent activation energy, red–ox

1. Introduction

Oxidative dehydrogenation of alkanes to alkenes is a promising route which may compete with the classical dehydrogenation due to more favourable thermodynamics. Alkenes are industrially obtained via catalytic dehydrogenation, which is a highly endothermic reaction and high temperatures ($T \geq 600^\circ\text{C}$) are used. By contrast, oxidative dehydrogenation is exothermic and therefore lower working temperatures are required. It is well known that catalytic oxidation generally obeys the reduction–oxidation mechanism [1], and the lattice oxygen of the catalyst plays an important role in the selective formation of olefins starting from their corresponding alkanes [2,3]. Several catalytic systems have been tested but up to now only few have shown good performances such as vanadium- [4–6] and molybdates-based catalysts [7]. Among these systems, nickel molybdate has been shown to be very active for ODH of light alkanes both in continuous and periodic flow systems [8–11]. Kinetics studies performed in continuous mode in the presence of NiMoO₄ evidenced that the olefin formation rate is independent of oxygen partial pressure [12].

In order to elucidate the role of lattice oxygen, propane oxidative dehydrogenation and catalyst re-oxidation were carried out separately using a pulse reactor. The different phases of the catalytic system (NiMoO₄) were tested varying temperature, propane partial pressure, gas pulses, reaction and re-oxidation times. The catalytic results were correlated to the reduction behaviour of the solid under hydrogen.

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2. Experimental

2.1. Catalyst preparation

A Mettler RC1 reaction calorimeter, was used to carefully control the experimental parameters (T , stirring speed, pH, etc.) which determine the structure and surface characteristics of the active catalyst [11].

The stoichiometric NiMoO₄ compound was prepared by coprecipitation from an equimolar molybdic acid and nickel nitrate solution (0.25 mol/l), 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 -NiMoO₄ formation. The β -NiMoO₄ phase was obtained *in situ* by thermal treatment of the α -phase up to 720°C and then cooling to the desired reaction temperatures. The α' -phase is obtained after heating beyond 720°C and complete cooling back to ambient temperature. The catalyst particle size was found to be in the range of 200–325 mesh.

2.2. Apparatus

The catalytic tests were carried out in a tubular quartz reactor (length 50 cm, internal diameter 1 cm) containing ca. 0.5 g of catalyst mixed with silicon carbide powder (ca. 10 g) in order to avoid severe gradients within the catalyst bed. The reaction apparatus was developed in order to separate the reduction from the oxidation steps and this was obtained by flushing the catalyst with inert gas between the two reaction steps.

The feed gas streams were metered with automated flow-meter controllers in order to maintain the same gas flow

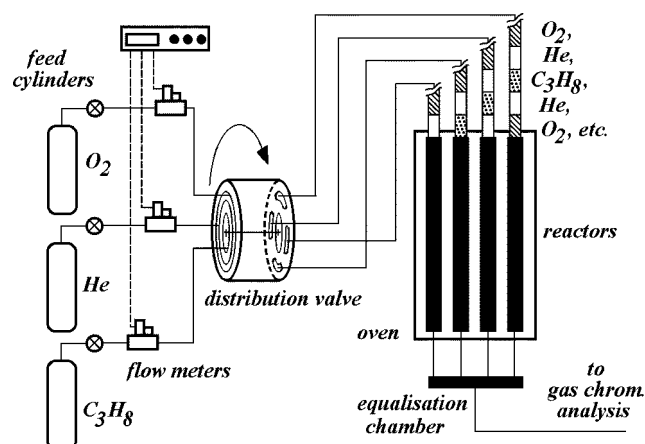


Figure 1. Scheme of periodic flow reactor apparatus. Each reactor, containing 0.5 g of catalyst, is fed continuously in the sequence $C_3H_8/He/O_2/He \dots$, the period between two successive positions of the gas distribution valve varying in the interval 0.25–120 s.

rate during each step. The gases were cyclically fed to the reactor in the following sequence: propane, helium (first flushing), oxygen and then helium (second flushing). The cycle frequency could be varied and the effect of the time on stream for each step (period) was investigated. In order to perform experiments with a wide range of periods and to avoid pneumatic disturbance due to the gas flows “stop and go”, four identical reactors were simultaneously used [11].

The system works in such a way that while two reactors are exposed to the helium washing, one is fed with propane (reduction phase) while the fourth is re-oxidised with oxygen (oxidation phase).

A rotating automatic distribution valve (see figure 1) was designed to operate according to the described four-steps sequence. The reactant gases from the four reactors were mixed and equalised in a chamber (volume 120 cm³, residence time ca. 1 min) prior to being analysed. The data obtained are representative of the overall conversions and selectivities, and are comprehensive of substances produced in the regeneration steps. The system – gas distribution valve, reactors and equaliser chamber – may be considered as a “black box” where with the same C_3 , O_2 and inert feeds, with the same amounts of catalyst and with the same T and P parameters, different conversion and selectivity can be obtained by only varying the period of the rotating distribution valve.

2.3. Analysis

The reaction products (CO_x , C_2H_4 , C_3H_6 and C_3H_4O) were analysed by gas chromatography. Oxygen and carbon monoxide were analysed using a molecular sieve 5A column (30 cm long with an internal diameter of 1/8 inch) connected to a thermal conductivity detector (TCD), ethylene, propene, propane and acrolein were separated and analysed by a porapak QS column (ca. 7 m long with an internal diameter of 1/8 inch) linked to both a flame ionisation (FID) and a thermal conductivity (TCD) detector.

2.4. 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 *iso-thermal reduction*) under a hydrogen atmosphere (gas feed 6 l/h) while recording the TG and DTG curves. For α - and α' -phases the samples were preheated in air up to the reduction temperature (T_r) and washed with helium. The β - $NiMoO_4$ phase obtained by thermal treatment of the α -phase up to 720 °C, is then cooled to the desired reduction temperature under air and finally washed with helium before the reduction.

BET surface areas were measured using a Micromeritics model 2200 instrument. FT-IR spectra (KBr discs) were recorded on a Nicolet 5PC spectrometer. XRD spectra were obtained with a Philips PW 1050 using Cu $K\alpha$ radiation.

2.5. Activity tests

The oxidative dehydrogenation of propane was carried out using α -, α' - and β - $NiMoO_4$ at temperature of 450–550 °C with a total flow of 3.6 l/h g_{cat} and with gas pulse periods of 0.25–120 s. With the 0.25 s period (short gas pulses), due to the axial diffusion in the pipes from the distribution valve to the reactors, the feed gas concentration reaching the reactor can be considered constant. The system can therefore be assumed to be pseudo-continuous (COS) and thus equivalent to a continuous system with mixed gas feed ($C_3/O_2/He$ 1/1/2).

When working with pulses longer than 20 s the interposed washing gas avoids reactants back-mixing and the system is operating in a true periodic mode (POS). Stationary conditions were checked by monitoring the invariability of the ΔT maximum excursion between the core temperature of the two reactors in phase opposition [11], and the experimental catalytic data were recorded for each period after 2 h.

3. Results and discussion

Figure 2 reports propane conversion and propene selectivity versus the pulse period at 480 °C. It can be observed that the increase of pulse period results in an increase of propene selectivity together with a decrease of propane conversion, and this is true for all the temperature ranges and with all studied phases.

Even if each catalyst phase is considered separately, and the results are compared at iso-conversion, increasing the period pulse still results in an increase propene selectivity. The data in table 1 indicate that the increase propene selectivity is not only due to a decrease in propane conversion (as in a consecutive reactions based pathway) but also depends on the separation of the oxidation–reduction steps.

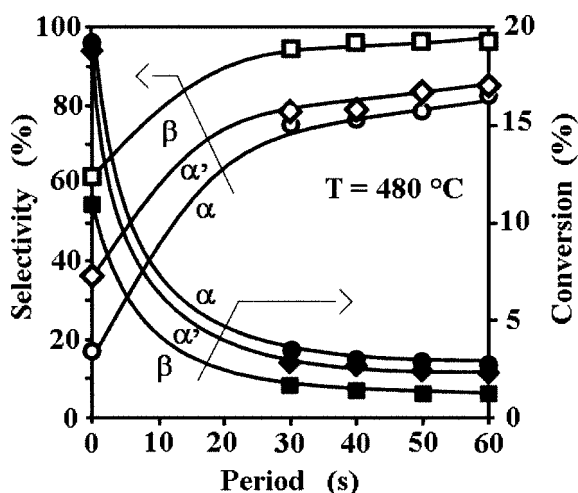


Figure 2. Propane conversion and propene selectivity versus the pulse period (at 480 °C).

Table 1

Selectivity data obtained on NiMoO₄ phases at various periods and temperatures.

Catalyst phase	C ₃ H ₈ conversion (%)	Temperature (°C)	Period (s)	C ₃ H ₆ selectivity (%)
α -NiMoO ₄	3.19	480	30	75.0
	3.21	500	60	84.3
	4.18	500	30	71.2
	4.11	520	60	80.0
α' -NiMoO ₄	2.33	380	0	76.0
	2.32	480	50	83.4
	3.54	500	30	74.4
	3.56	520	60	82.7
β -NiMoO ₄	1.13	380	0	91.6
	1.16	480	60	96.1
	2.11	500	30	93.7
	2.56	540	60	94.8

This means that the oxygen monolayer plays an important role in propane ODH to propene.

In all cases (COS, POS 40 s and POS 60 s), the α - and α' -phases show higher propane conversions with respect to the β -phase both in COS and POS mode (see figures 3, 4 and 5). It can be also noticed that with a temperature increment of 40–60 °C the β -phase can reach the same propane conversion obtained with α - and α' -phases.

As previously reported [11], the apparent activation energy of propane conversion is lower in POS mode with respect to the continuous (COS) mode. For all the three phases the activation energies obtained with the POS mode were found to be lower (54.3–62.7 kJ/mol) with respect to those obtained with the continuous mode (COS), the less selective method (104.5–125.4 kJ/mol).

Apparent activation energy values were found to be ca. 46–50.2 kJ/mol for the catalyst reduction under hydrogen. The correlation between the activation energy of reaction in POS mode (54.3–62.7 kJ/mol) and that of solid reduction under hydrogen (46–50.2 kJ/mol) provides strong

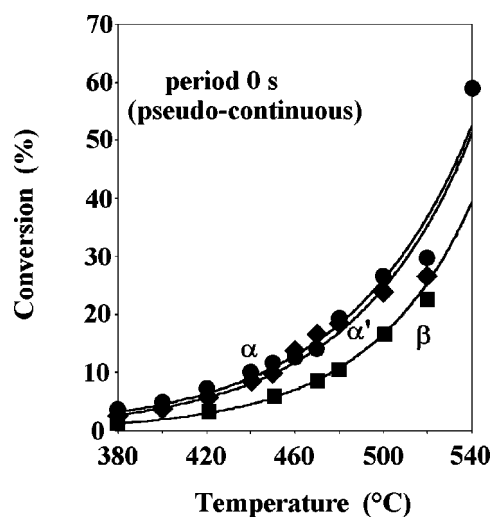


Figure 3. Propane conversions for α -, α' - and β -phases in pseudo-continuous (COS, i.e., period 0 s) mode.

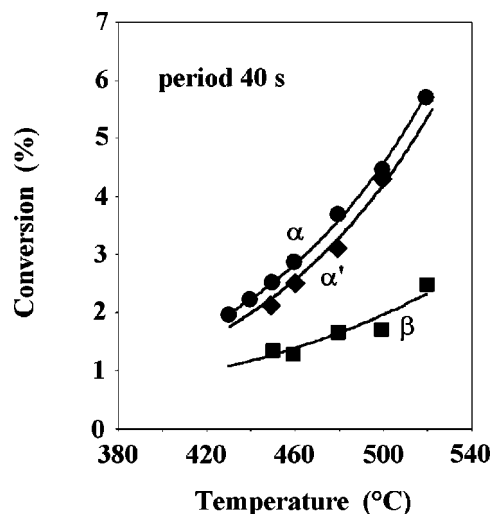


Figure 4. Propane conversions for α -, α' - and β -phases in periodic (POS with period 40 s) mode.

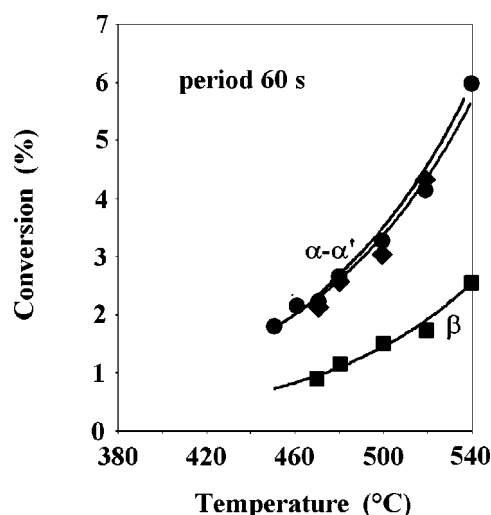


Figure 5. Propane conversions for α -, α' - and β -phases in periodic (POS with period 60 s) mode.

Table 2
Comparison of NiMoO₄ phases performances at iso-conversion.

Catalyst phase	C ₃ H ₈ conversion (%)	Temperature (°C)	Period (s)	C ₃ H ₆ selectivity (%)	C ₃ H ₆ intrinsic yield (mmol/h m ²)
α -NiMoO ₄	2.24	450	30	72.3	0.079
	2.50	470	40	77.8	0.094
	2.57	480	60	82.4	0.103
α' -NiMoO ₄	2.33	380	0	76.0	0.237
	2.44	470	30	78.2	0.255
	2.53	480	40	78.1	0.265
	2.32	480	50	83.4	0.260
β -NiMoO ₄	3.21	420	0	78.7	0.338
	2.11	500	30	93.7	0.324
	2.56	540	60	94.8	0.364

evidence for the suggestion that the reaction is governed by a *red-ox* mechanism.

A quantitative comparison of all the studied catalyst phases, shows that the β -phase is always the most selective one with respect to propene (see table 2). Expressing the catalytic performances of the different phases in terms of intrinsic propene yield it appears that the β -phase is the most interesting catalytic system.

The specific surface area (S_{BET}) of the different phases is 33 m²/g for the α -phase and 12 m²/g for both the β - and α' -NiMoO₄ phases. The S_{BET} area reduction, due to the $\alpha \rightarrow \beta \rightarrow \alpha'$ -NiMoO₄ phase transformations, is also accompanied by a significant change in the morphological texture of the catalysts surface [14].

In order to gain a deeper understanding of the differences between NiMoO₄ phases and the involvement of the lattice oxygen during propane ODH, hydrogen reduction tests were performed on the three phases at constant temperature (ITR). The *in situ* treatments of each phase are summarised in the tables reported in figure 6. For each phase noticeable differences in terms of reduction rate vs. temperature are found. These variations are due to the oxygen mobility that increases with temperature. At different temperatures a comparison of the reduction trends of the three phases shows that the depletion rate of β -NiMoO₄ is the highest. It should be also noticed that although α' - and α -NiMoO₄ have the same structure, the α' -NiMoO₄ obtained after cooling the β -NiMoO₄ back to room temperature, has higher reduction rate than the α -NiMoO₄.

The importance of the relationship between the selective oxidation ability for olefin production and the mobility of lattice oxide ions of composite metal oxide catalysts has been reported by many research groups. However, in this study the correlation of TG analyses and catalytic activity obtained with the different phases of NiMoO₄ suggests that the reaction properties are related to the extent of the oxygen vacancy on the catalytic surface. In a previous study [9], electrical conductivity measurements performed on NiMoO₄ phases evidenced two types of vacancies. The oxygen vacancies of the α -phase have been found

to be ionised twice while the corresponding vacancies in the β -phase were ionised once.

As commonly reported for oxidative dehydrogenation of light alkanes in pulse reactors, in the periodic pulse reactor (POS) the rate of oxygen depletion diminishes when the surface is deeply reduced. The depletion layer depth depends on the pulse period: longer periods yield higher average reduction. Basically two hypotheses could be made: the first one considers the depletion rate vs. time as independent of the already consumed oxygen, the second hypothesis considers the depletion as dependent on the surface oxygen abundance. Figure 7 shows the theoretical change of depletion rate with the pulse for cycles of 10 and 40 s periods, respectively. In the former case the single 40 s pulse conversion of propane would thus be a multiple of the single pulse conversion of the shortest periods (i.e., the 40 s pulse period conversion is four times the 10 s pulse period conversion value). In the second case, the single 40 s pulse conversion would be minor than four times the 10 s pulse period conversion value. Therefore, in the first hypothesis, the overall conversion should be independent of the period, while in the latter hypothesis the overall conversion decreases when the period increases. Our experimental data support the second hypothesis.

In order to evidence the oxygen type for the different phases of NiMoO₄, a study of the reduction rate ($-DTG$) versus the extent of the reduction has been performed. The tests, performed at constant temperatures under hydrogen instead of propane (in order to avoid problems related to carbon formation), and some structural considerations may help to elucidate the type of lattice oxygen and its activity. The lattice oxygen extracted from the solid, as reported by Haber for CoMoO₄ phases [15], is not necessarily the same as that reacting when the catalyst is exposed to propane.

The TG and DTG data vs. time, obtained using thermogravimetric technique, are combined in such a way that the reduction rate ($-DTG$) is plotted vs. specific oxygen depletion. Figure 8 reports the reduction profile of the different phases of the catalysts at different temperatures. In all cases the deconvolution of the reduction profile curves

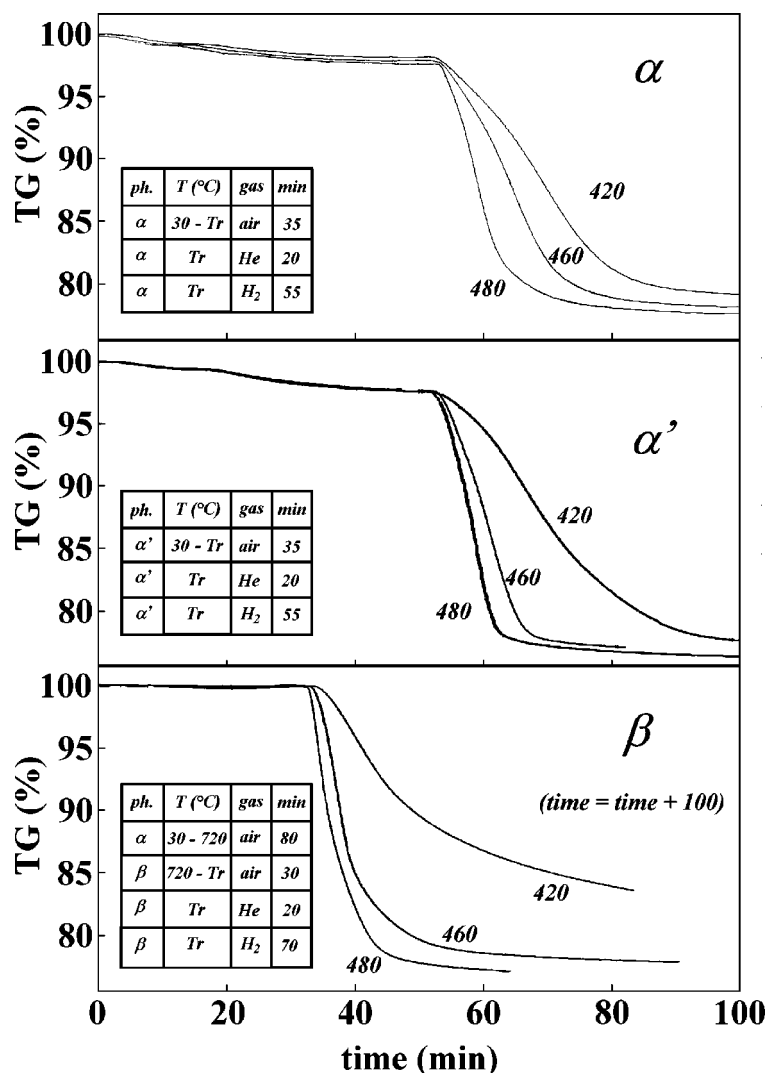
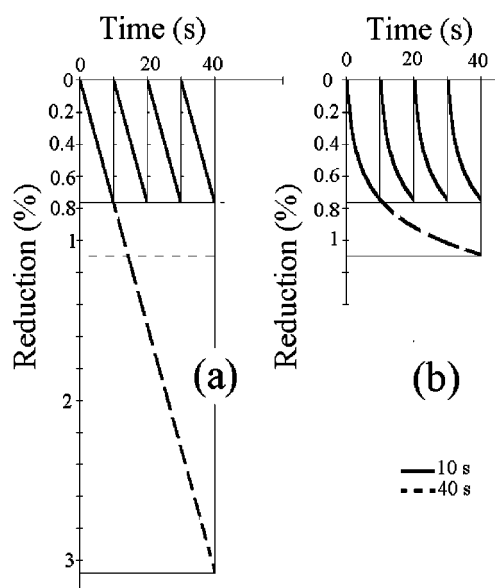
Figure 6. Iso-thermal reduction tests (ITR) for α -, α' - and β -NiMoO₄ under hydrogen (see experimental).

Figure 7. Theoretical oxygen depletion change with pulse for cycles of 10 and 40 s period, respectively.

reveals the presence of two partially overlapped peaks probably due to the existence of two reduction steps. It can also be noticed that the trend of the β -phase is different from that of the α - and α' -phases.

Assuming that the two observed peaks correspond to two oxygen types involved in the reduction step, i.e., extracted consecutively, the profile of the TG vs. time curves and that of the $-DTG$ vs. $-TG$ curves should be similar to those reported in figure 9. The exemplified behaviour implies that the reduction slope and its duration correspond to two separate DTG peaks which indicate a consecutive depletion of different types of oxygen. These observations ($-DTG$ vs. $-TG$) provide information on both the reduction rate, and the extent and type of oxygen (M-O bond broken).

Experimentally (figure 8) it is clear that a superposition of the two peaks occurs, with an inversion in reduction tendency for the β -phase. These peaks can be attributed to two different types of M-O (*a priori* Ni-O and Mo-O) bonds in the NiMoO₄ system.

Propane ODH on the Ni-Mo-O system has been widely investigated and the reaction rate constant, the partial order

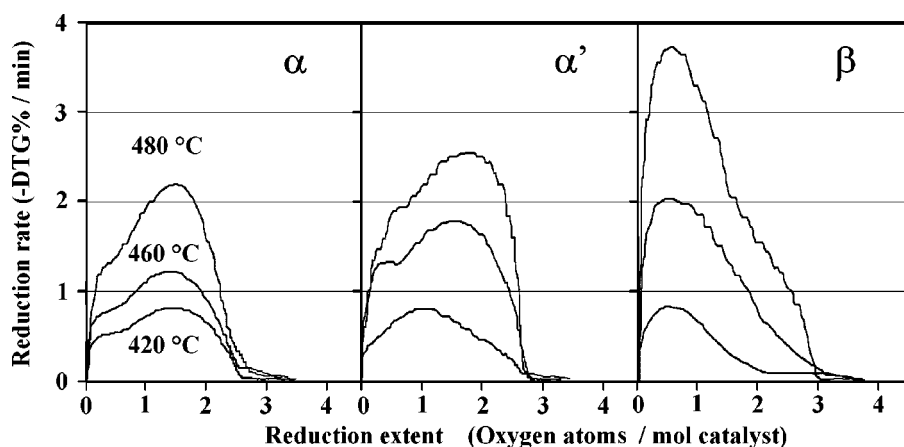


Figure 8. Reduction profile (rate vs. degree) for the α -, α' - and β -phases at 420, 460 and 480 °C.

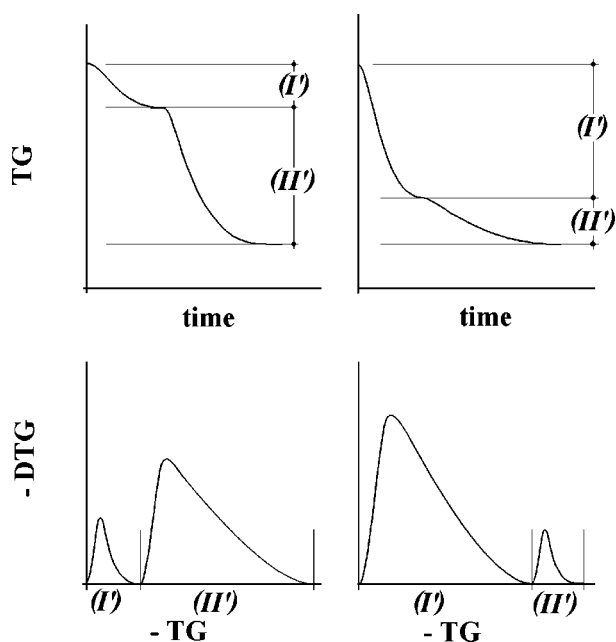
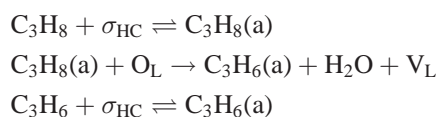


Figure 9. Trends of the TG vs. time and ideal reduction profiles for an hypothetically consecutive depletion of two different types of oxygen.

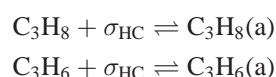
with respect to propane and to oxygen have been reported for a continuous flow reactor system [12,16]. These studies have shown that propene formation is unaffected by the partial pressure of oxygen. Therefore, to elucidate the respective role of the lattice oxygen in propane ODH and of the molecular oxygen for restoring the catalyst lattice oxygen employed during the reaction, the periodic flow equipment is useful as it allows the two steps (catalyst reduction and re-oxidation) to be separated.

Four different steps can be considered during the propane periodic ODH:

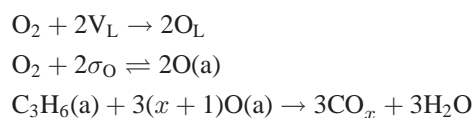
Step 1 (propane feed)



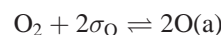
Step 2 (first He flushing)



Step 3 (oxygen feed)



Step 4 (second He flushing)



As it was mentioned by Stern and Grasselli [16], in the above equations, σ_{HC} and σ_{O} denote, respectively, the hydrocarbon and oxygen adsorption sites, (a) an adsorbed species, O_{L} and V_{L} lattice oxygen and lattice oxygen vacancy, CO_x deep oxidation waste products.

The partial oxidation of propane occurring during step 1 can be described by a Mars–van Krevelen mechanism. In this step it is possible to consider propane and propene in adsorption equilibrium, and the propene surface coverage is expected to be small. The rate of propene formation is zero order with respect to oxygen [11,12].

In contrast, during step 3 the deep oxidation of propylene to CO_x follows a Langmuir–Hinshelwood mechanism. The rate of by-products formation is half-order in oxygen. The last reaction can obviously occur only if the adsorption equilibrium in step 2 is not completely left evolved.

Similarly, if some oxygen adsorbed species $\text{O}(\text{a})$, residual from step 4, reach step 1, the undesired reaction of combustion may occur.

Propene desorption is a key-step for selectivity determination and this may be related to the acid–base surface sites. In fact basic promoters such as potassium and calcium oxides have been found to increase the desorption of propene formed and consequently its selectivity [17].

Indeed, in order to maintain a good propene selectivity, it is also of importance that the flushing steps are carried out with appropriate time and efficiency.

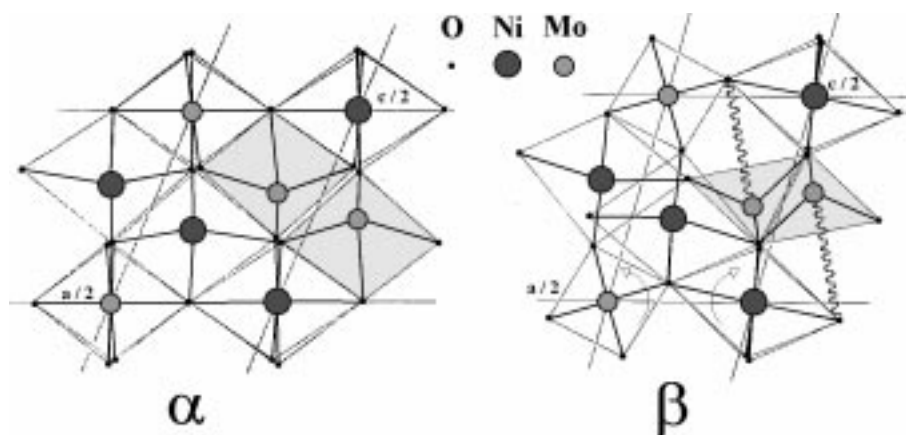


Figure 10. Partial view of the crystal structure of α - and β -NiMoO₄ phases.

The lattice oxygen mobility (i.e., nucleophilic oxygen), in terms of relative velocity of the reactions of depletion and restoring lattice oxygen, plays an important role, if we compare the restoring lattice oxygen occurrence and the competitive and/or consecutive reaction that leads to chemisorbed oxygen (i.e., electrophilic oxygen).

Using a periodic flow system it is possible to evidence that with deep oxygen depletion re-oxidation of the catalyst may not be enough to fully restore the oxygen vacancies generated during the reaction. As a consequence chemisorbed oxygen surface coverage may result low or even null. Catalytic results suggest that, when the periods become longer, the adsorbed oxygen leading to complete oxidation is limited, and the selective lattice oxygen lead to a higher propene formation. However, it cannot be excluded that at least a small non-selective [18] part of lattice oxygen, that can be removed when the pulse periods become longer, can be present in the solid.

As the results obtained on the two phases of NiMoO₄ are different this implies that the type of lattice oxygen and the type of vacancies involved in propane ODH may be different.

The NiMoO₄ polymorphic system is monoclinic with space group C2/m. Only α - and α' -phases can be observed at normal temperature and pressure (NTP) conditions. The α - and α' -phases, which are stable from ambient temperature up to 650 °C, present the structure of α -CoMoO₄ [19,20] with molybdenum in a distorted octahedral site. While the β -phase, which is stable between 250 and 650 °C, presents the structure of α -MnMoO₄ [21] with molybdenum in a distorted tetrahedral site.

Using crystallographic notation [22], a representation of the polyhedra surrounding the metal atoms is given in figure 10, where a partial view of the crystal structure of both α - and β -phase NiMoO₄ shows some similarities and differences; the general arrangement of metal atoms in the two structures is the same (although the oxygen-atom positions are considerably changed) but the most important change is in the Mo–oxygen coordination. In the α -phase all the Mo is in a highly distorted octahedral coordination whereas in the β -phase the two crystallographically independent Mo

atoms are each located at the centers of somewhat irregular tetrahedra (grey coloured cells). Accordingly in the β -phase the Mo is in both octahedral and tetrahedral coordination. The Ni atoms are always located within irregular octahedra of oxygen atoms both in α - and β -phases.

The most striking feature in the structural change from α - to β -phase is hence the change in coordination of some Mo atoms. Such a change is accompanied by cleavage of some Mo–O bonds (represented as wavy line), a slight rotation of Mo and Ni octahedra and a variation of the cell angle and volume.

The fact that some of Mo–O bonds are broken when the transition from the α - to the β -phase occurs [14], implies that the selective formation of propene could be explained by this oxygen mobility.

However, another type of oxygen source may be given by Ni–O bonds even if the Ni–oxygen coordination is the same in the two phases. The volume cell changes, together with the Mo modification of oxygen surrounding imply that at least a slight distortion of the network weakens some Ni–O bonds. In fact figure 8 evidences two reduction peaks with a corresponding amplitude ratio of ca. 1–1.5/3–2.5. When the transition from α - to β -phase occurs the appearance with time of the two reduction peaks and their extents seem to be inverted. Therefore if one peak is attributed to the reduction of Ni–O bonds and the other one to the Mo–O bonds, the latter seem to be less stronger than Ni–O in the β -phase and moderately stronger in the α -phase. This hypothesis may be in line with the experimental data on M–O bonds reported in the literature [20,22]. The average bond length of Mo–O in an octahedral coordination is 1.99 Å while in a tetrahedral coordination it is 1.76 Å. The Ni–O bond lengths in the two phases, where the oxygen surrounding is octahedral, are ca. 2.09 Å.

The phase transformation kinetics of NiMoO₄ systems has been studied and it evidenced the relation between the extent of β -phase formed with time and calcination temperature [9]. Other authors have pointed out that the occurrence of phase transition can be achieved by catalyst ageing with time under the studied reaction conditions [14,23,24]. This phase transformation seems to be facilitated during

oxidation–reduction steps. Therefore, the surface oxygen vacancies relate in part to the type of oxygen involved in $\alpha^- \rightarrow \beta$ -phase transformation which can be removed and replaced during the reduction–oxidation steps. The system can evolve towards a more stable oxygen form with reaction time leading to a structural transformation beginning at the surface and migrating in the deep.

In our opinion these differences in terms of oxygen coordination of the Mo and Ni may explain the various reduction behaviour of the NiMoO₄ phases and the corresponding propene selectivity. We believe that the lattice oxygen involved in selective propylene formation is a bridged Ni–O–Mo oxygen, probably the type of oxygen which is involved when balancing from α^- to β -phase.

4. Conclusion

Oxidative dehydrogenation of propane was carried out under steady state conditions with a periodic flow reactor system on α^- , α' - and β -NiMoO₄ catalysts.

The apparent activation energy of α^- , α' - and β -phases measured by catalyst reduction under hydrogen at different temperatures fits well with the corresponding values obtained in propane ODH reaction performed with a periodic flow reactor.

Reduction tests at constant temperature of the different phases, performed under hydrogen in the range of reaction temperatures and monitored by TG analyses showed that with the β -phase lattice-oxygen-consumption rate is faster than on the α^- and α' -phases.

The rate of reduction, as function of oxygen depletion extent, evidenced different sources and content of lattice oxygen in the catalyst depending on the nature of NiMoO₄ phases. The reduction behaviour of each phase was correlated with its corresponding catalytic activity.

The intrinsic propene yield obtained with different NiMoO₄ phases has shown that the β -phase is the most interesting. Indeed the β -phase shows an inversion in metal–oxygen reduction behaviour.

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