On the $NiMoO_4$ oxidative dehydrogenation of propane to propene: some physical correlations with the catalytic activity

C. Mazzocchia [1], C. Aboumrad [1], C. Diagne [1], E. Tempesti [2], J.M. Herrmann [3] and G. Thomas [4]

[1] *Dipartimento di Chimica Industriale e Ingegneria Chimica, Politecnico di Milano, P.za L. Da Vinci 32-20133 Milano, Italia*

[2] *Dipartimento di Ingegneria Meccanica dell'Università di Brescia, Via Valotti 9-25060 Brescia, Italia*

[3] *Ecole Centrale de Lyon, URA au CNRS Photocatalyse, Catalyse et Environment 69131 Ecully Cédex, France*

[4] *E.N.S.M. de Saint Etienne, 158 Cours Fauriel, 42023, St.Etienne Cédex, France*

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The α- and β-phases of $NiMoO_4$ have been investigated with different techniques (X-ray diffraction, electrical conductivity, IR spectroscopy) in order to tentatively rationalise the different catalytic activities observed in the oxidative dehydrogenation of propane to propene. XRD analyses have shown that at 595 °C, the β-phase is already present but a temperature of $\sim$ 700 °C is required to obtain a full conversion into a pure β-phase. Electrical conductivity showed the presence of anionic vacancies. It is proposed that propene is formed by the reaction of propane with surface O^{2-} anions. The β-phase is almost twice more selective in propene formation than the α-phase for comparable conversion at identical temperatures. This could derive from different oxygen environments on the active catalytic site.

Keywords: Propane dehydrogenation; nickel molybdate; $NiMoO_4$ propene formation

1. Introduction

The selective oxidations of lower alkanes are becoming increasingly important both in fundamental and in industrial chemistry. Most of the work published up to now on partial oxidation using gaseous oxygen as an oxidant refers to the oxidation of butane since its total oxidation to maleic anhydride is the only process which is highly selective and operative [1]. For propane dehydrogenation, typical oxidation catalysts are, among others, bismuth, cobalt and nickel molybdates [2–4]. The catalytic properties of these molybdates are closely

related to their structure which depends on the method of preparation and on the thermal treatment.

The preliminary activation of the C-H bond may involve different possibilities which are respectively:
- hydride abstraction [5]
- participation of lattice oxygen [6]
- heterolytic or homolytic bond dissociation [7]
- concerted mechanism [8].

In the present study, we intend to further elucidate the properties of the 2 different phases in the Ni-Mo-O system which, according to its chemical and phase composition, possesses different activities in the oxidative dehydrogenation of propane to propene [4].

2. Experimental

It is known from the literature that $NiMoO_4$ may exist in three different structures. The two phases which are stable at atmospheric pressure are called hereafter α- and β-phases.

The primary difference between these phases is the co-ordination of molybdenum: octahedral in the α-phase and tetrahedral in the β-phase. It is also known that the β-phase of $NiMoO_4$, unlike the isotypic phase of $CoMoO_4$, cannot be quenched at ambient temperature.

1. *Catalysts preparation:* a 0.25 M solution of $Ni(NO_3)_2 \cdot 6\ H_2O$ (pH 4.7) and an equal amount of 0.25 M solution of $H_2MoO_4 \cdot H_2O$ in aqueous ammonia (pH 5.6) were mixed at 85 °C. The precipitation was allowed until pH 4.9. The precipitate was filtered at 85 °C and dried at 110 °C for 4 hrs. [9,10].

The α-phase has been obtained by heating the precursor at 550 °C for two hours under normal atmosphere. The purity of the prepared α-$NiMoO_4$ was checked by Raman spectroscopy to verify the absence of MoO_3.

The surface areas were measured using the BET method. The value of the specific surface area of the α-phase is equal to 40 m^2/g Since the β-phase cannot be quenched at room temperature, its surface area cannot be measured and is assumed to be equal to that of the α-phase reobtained after cooling down of the β-phase at room temperature [9].

2. *High temperature X-rays diffraction experiments:* high temperature X-rays diffraction experiments have been carried out in air using a Siemens D501 diffractometer. A linear counter ELPHYSE associated to a 4096 channel card connected to a PDP 11/24 computer allowed fast data acquisition. Such an equipment is necessary to follow kinetics of reactions in satisfactory conditions [11].

A series of X-ray experiments has been performed to define the exact conditions of formation of β-nickel molybdate. Within the frame of these conditions electrical conductivity measurements and catalytic tests have been carried out on pure α- or β-nickel molybdate.

3. *Electrical conductivity measurements:* they were carried out in a cell of the static type described in ref. [12]. The catalysts were slightly compressed between two platinum electrodes ($P \sim 10^5$ Pa), thus enabling good contacts between particles without modifying the texture.

4. *Infrared spectroscopy:* the spectra (KBr) were recorded using an FT-IR 1720 spectrometer (Perkin-Elmer).

5. *Catalytic tests:* they were carried out as already reported [4]. It should be emphasized that the catalytic tests on the β-$NiMoO_4$ phase have been carried out first by heating α-$NiMoO_4$ catalysts at 700 °C in oxygen flow for 15 min in order to complete the $\alpha \rightarrow \beta$ transition and then by cooling to the predetermined reaction temperature ($T > 300$ °C) at which no $\beta \rightarrow \alpha$ phase transition occurs [9].

3. Results and discussion

X-RAYS DIFFRACTION EXPERIMENTS

Stoichiometric α-$NiMoO_4$ has been heated under atmospheric conditions at a rate of 20 °C min^{-1} from the room temperature to a temperature Tw_1. After one minute, a diffractogram was acquired in four minutes and saved. Then the sample was heated again at the same rate up to a new value Tw_2, and studied in the same condition. X-ray diffractions of samples heated at Tw_i equal to 595, 620, 640, 665, 675, 695 °C have been analyzed (fig. 1). Under those dynamic conditions, it is clear that the phase β is already present at 595 °C, but the phase α has not fully disappeared at 695 °C after 3 minutes. So kinetics of the transformations are to be studied.

The conversion degree λ of the reaction $\alpha \rightarrow \beta$ has been followed under isothermal conditions at 625, 640 and 675 °C. An estimate of this degree was given by the ratio of the intensity of peak of the phase β ($d = 3.34$ Å) during the experience to the same intensity obtained after a treatment at 760 °C during 5 min performed once the experiment is finished, and a return to the conditions of the experiment. At 760 °C, the phase β is always pure, and the return to the temperature at which the experience was done allows us to avoid corrections of the Debye factor. The reaction is very sensitive to the temperature (fig. 2). The

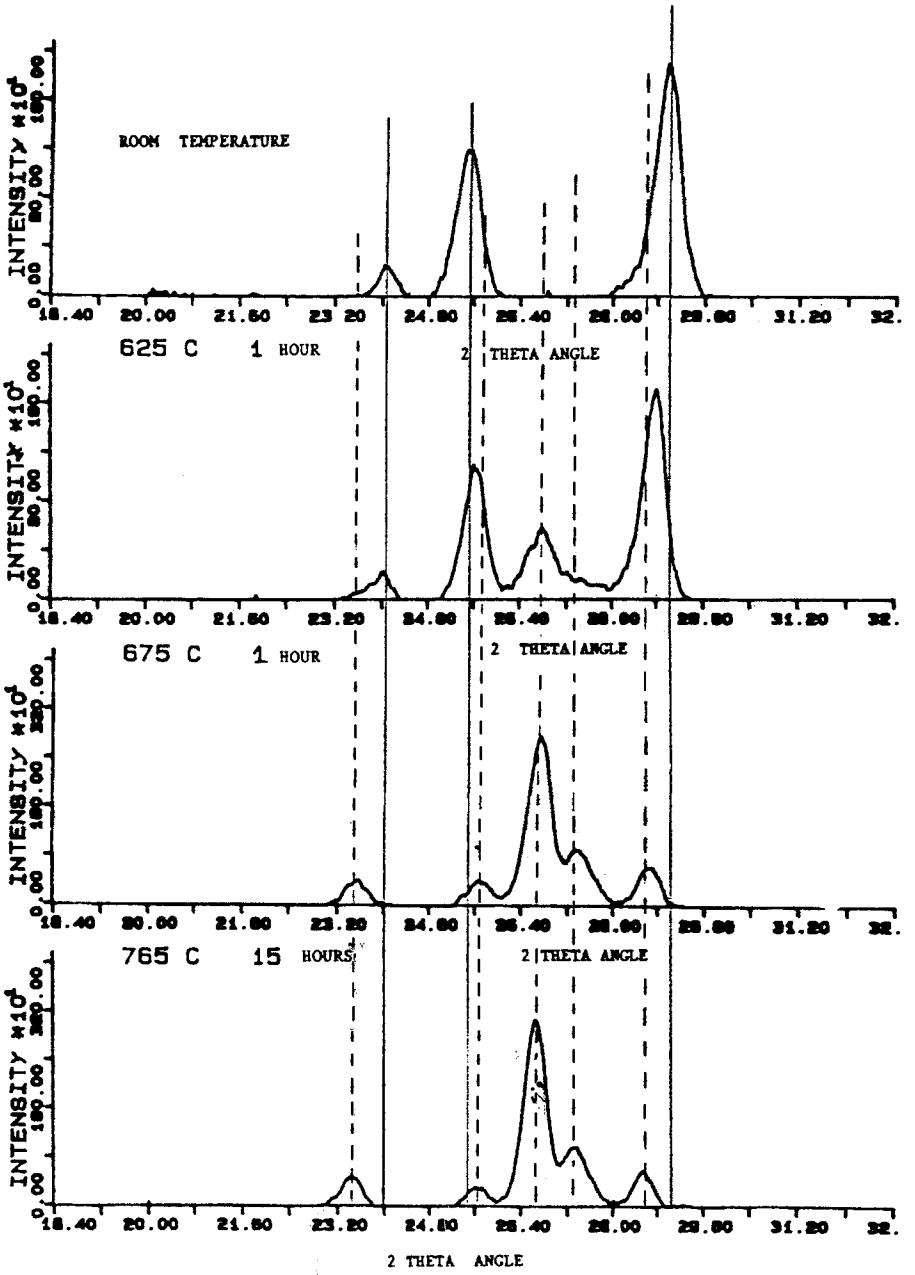

Fig. 1. Diffraction traces of stoichiometric $NiMoO_4$. Solid line: α-phase (refs. [18] and [19]); dashed line: β-phase (ref. [19]).

rate is very high just in the beginning of the isotherm, but the yield of reaction presents a very small variation after one hour, and it is strongly related to temperature (625, 675 ° C).

ELECTRICAL CONDUCTIVITY MEASUREMENTS

α-phase

The electrical conductivity σ of the phase α was measured as a function of temperature ($440 \leqslant T \leqslant 500\,^{\circ}$C) (fig. 3) and oxygen pressure ($1.3 \leqslant P_{O_2} \leqslant 52.6$ kPa) (fig. 4). The conductivity varied according to the experimental law:

$$\sigma = \sigma_0 \cdot \exp(-\Delta H_a/RT) \cdot P_{O_2}^{-1/n} \tag{1}$$

with an enthalpy of conduction ΔH_a equal to 133,8 kJ · mol^{-1} and $n \approx 5.7$.

The value of the exponent is close to the integer 6. This means that the main surface defects are compatible with the model of doubly ionized anionic vacancies $V_0^{\cdot\cdot}$, which are in equilibrium with oxygen according to the equation:

$$\tfrac{1}{2}O_2(g) + V_0^{\cdot\cdot} + 2\,e^- \Leftrightarrow O_0^{\times}. \tag{2}$$

As a consequence, the labile oxygen species on α-$NiMoO_4$ in equilibrium with the gas phase are normal oxygen anions located on the surface $O_0^{\times}$. With respect to the results obtained with α-$NiMoO_4$, they can constitute oxygen active species in the oxidative dehydrogenation of propane to propene.

Their regeneration would consist in the spontaneous reoxidation of the surface by gaseous O_2 (eq. (2)) according to a Mars and Van Krevelen mechanism.

β-phase

Conductivity measurements were performed on β-$NiMoO_4$ obtained after heating the α-phase in the conductivity cell at 700 ° C during 900 s and cooling at the desired temperature chosen in the range 440–500 ° C. As shown in figs. 3

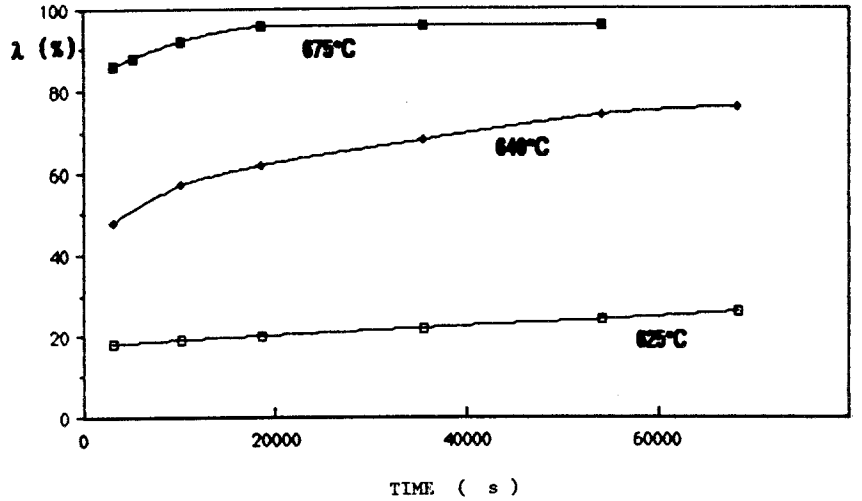

Fig. 2. Kinetics of the transformation $\alpha \rightarrow \beta$-$NiMoO_4$ followed by X-ray diffraction analysis (conversion λ (in %) as a function of time).

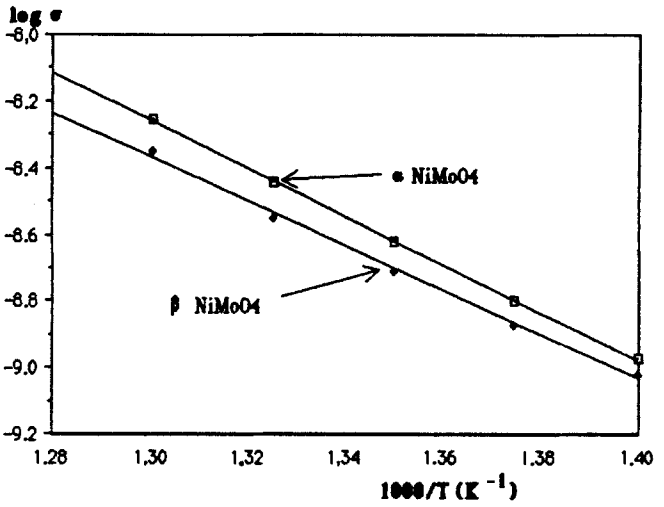

Fig. 3. Electrical conductivity variations as a function of temperature (Arrhenius plot).

and 4, the conductivity of the β-phase follows the same laws as the α-phase for oxygen pressure $P_{O_2} \geqslant 19.7$ kPa. The value of ΔH_a is equal to 125.4 kJ and that of n close to 4. So, it can be concluded that the major defects in β-$NiMoO_4$ are anionic oxygen vacancies, singly ionized. Both α- and β-$NiMoO_4$ exhibit an n-type semiconduction and for the β-phase:

$$V_0^{\cdot} + e' + \tfrac{1}{2}O_2 \Leftrightarrow O_0^{\times}. \tag{3}$$

INFRARED SPECTROSCOPY

It has been reported by Chaar and his colleagues that the V_2O_5/MgO catalyst system shows appreciable activity and selectivity for the oxidative dehydrogenation of propane [13] and butane [14]. This has been attributed to the absence of V=O bonds found in pure V_2O_5 which cause the formation of oxygen containing products. Recent results [15] seem to confirm that selective oxidation of ethane and propane over alkali and alkaline earth orthovanadates, due to the absence of V=O species, mainly depends on the strength of the V-O-V bond.

Referring now to the MoO_3/NiO system we are not aware of specific correlations between infrared absorptions and catalytic activities in the oxidative dehydrogenation of alkanes. At this regard some references can be cited with respect to pure MoO_3 and MoO_3/CoO which is characterized by phase-transition effects similar to those reported for MoO_3/NiO. As for MoO_3, the band at 980 cm^{-1} is normally attributed to the Mo=O bond while the bands at 870 and 812 cm^{-1} are attributed to Mo-O- bonds. Any shift of the band having the nature of a double bond to lower frequencies implies a decrease in the

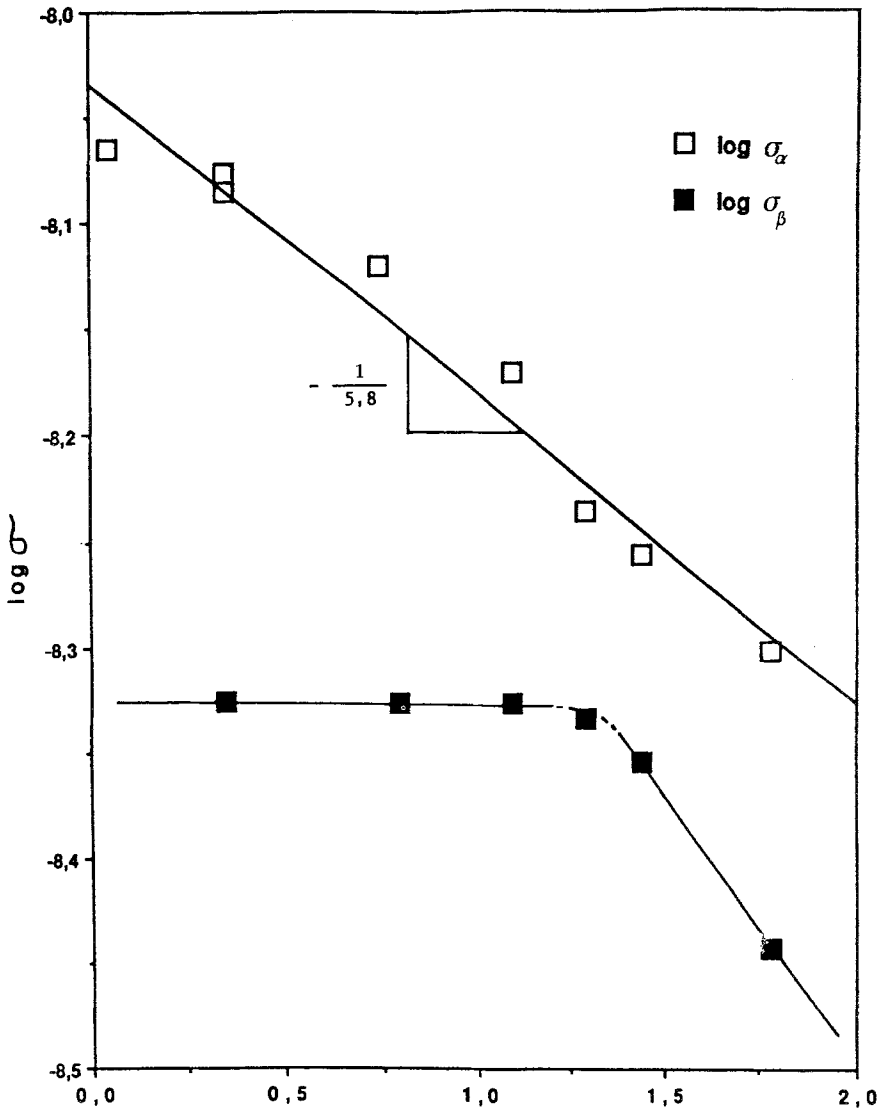

Fig. 4. Variations of the electrical conductivity as a function of oxygen pressure (in kPa) ($T = 500\,^\circ$C).

characteristics of double bond and an increase in the labilization of the bond itself [16].

Similar shifts occur with $CoMoO_4$. Indeed with green $CoMoO_4$ there is a strong absorption band at 945 cm^{-1} which is typical of the octahedral configuration of Mo. For violet $CoMoO_4$, based on ATR techniques and assuming that

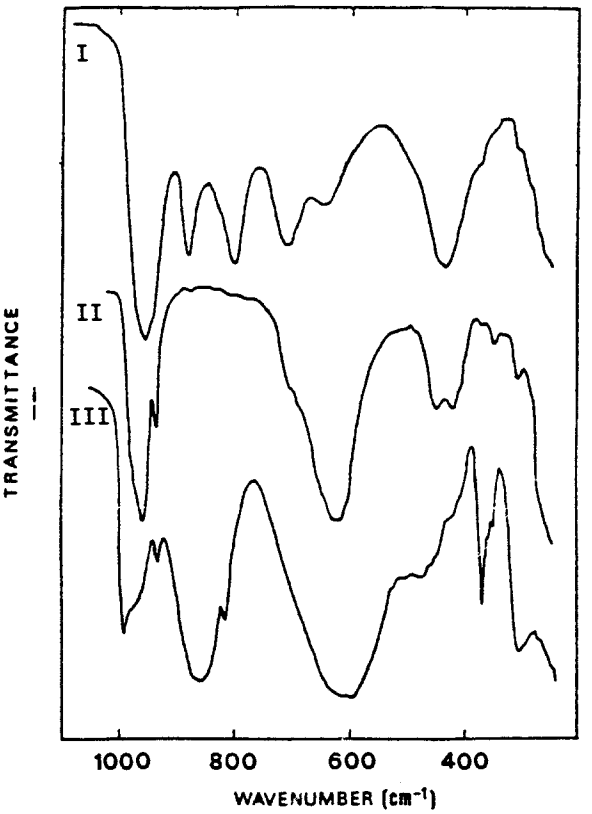

Fig. 5. IR spectra of α- and β-$NiMoO_4$ phases.

the observed differences of band intensities cannot be justified by different energy dispersions between IR and ATR techniques, the shift is even greater (at 930 cm^{-1}) while two novel absorptions at 840 and 780 cm^{-1} become evident. A tetrahedral coordination is assumed for Mo together with the possibility of absorption of the second metal [17]. Significantly, when considering the results obtained in the oxidative dehydrogenation of 1-butene, green α-$CoMoO_4$ gives only traces of 1,3-butadiene, whereas the violet β-phase gives small but significant quantities of the same products.

Pure β-$NiMoO_4$ cannot be obtained at room temperature as β-$CoMoO_4$ because it is not metastable. Fig. 5 typically refers to β-$NiMoO_4$ solid solution stabilized [10] with excess NiO (I), pure α-$NiMoO_4$ (II), $NiMoO_4 \cdot 5\ MoO_3$ (III). Stabilized β-$NiMoO_4$ (I) exhibits at ca 950 cm^{-1} an absorption band and two novel absorption bands at ca. 880–800 cm^{-1} which are characteristic of β-$NiMoO_4$.

It may be seen that when passing from (III) to (II) to (I) the striking differences observed may be rationalized in view of the discussion reported above. Considering the different catalytic activities of α- and β-$NiMoO_4$ re-

Table 1
Catalytic activities of both $NiMoO_4$ phases at various temperatures

Catalyst $NiMoO_4$ phase	Temperature (°C)	Conversion (%)	Activity in C_3H_6 (mmol/h)	Intrinsic activity in C_3H_6 (mmol/h/m^2)
	500	9.6	4.7	0.23
α	530	15.2	7.0	0.35
	560	24.8	9.2	0.46
	500	7.2	5.6	0.75
β	530	12.5	9.2	1.23
	560	20.85	13.2	1.76

Feed: 15% C_3H_8 + 15% O_2 in N_2.
Total feed 15 l/h for 500 mg of catalyst.

ported in this work, for the latter catalyst we postulate a multifunctional (Ni-O-Mo linkages) nature of the active site for propane oxidative dehydrogenation.

Catalytic results

Both α- and β-phases characterized above were tested in the oxidative dehydrogenation (OXD) of propane into propene at different temperatures. All the catalytic results (activity, conversion an selectivities) are listed in tables 1 and 2 It appears that the overall conversion is of the same order for both phases. However, the selectivity in propene formation for the β-phase is almost twice as big as that of the α-phase, propene remaining the major reaction product in the two cases. Moreover, the intrinsic activity (in mol/h/m^2) of the β-phase is ca. 3.5 bigger than that of the α-phase. Electrical conductivity measurements versus P_{O_2} have shown the presence of anionic vacancies in the surface lattice of nickel molybdates. The formation of propene can proceed via

Table 2
Selectivities in various oxidation products at various temperatures

Catalyst $NiMoO_4$ phase	Temperature (°C)	Conversion (%)	Selectivities (%)					
			CO	CO_2	C_2H_4	C_3H_6	CH_3CHO	CH_2CHCHO
	500	9.6	23.0	21.4	2.0	49.0	0.6	4.0
α	530	15.2	27.0	21.0	2.0	46.2	0.5	3.0
	560	24.8	32.2	24.6	2.0	37.5	0.2	3.0
	500	7.2	10.3	8.0	0.7	78.1	0.3	2.5
β	530	12.5	12.0	10.1	1.0	73.0	0.7	3.0
	560	20.85	18.0	14.0	1.3	63.1	0.3	3.5

Feed: 15% C_3H_8 + 15% O_2 in N_2.
Total feed 15 l/h for 500 mg of catalyst.

the formation of such vacancies by reaction with O^{2-} surface anions according to the reaction:

$$C_3H_8 + O_S^{2-} \rightarrow C_3H_6 + H_2O + V_0^{\cdot\cdot} + 2e^-. \quad (4)$$

The difference in propene selectivities can be attributed to a difference in reactivity of lattice O^{2-} anions present at the surface of both phases; this may arise from different oxygen environments on the active catalytic site (see infrared evidences).

4. Conclusion

It has been demonstrated by different techniques (X-ray analysis, electrical conductivity, IR spectroscopy) that the two phases of $NiMoO_4$ (α and β) are significantly different. The same phases differ also in terms of catalytic activity. The β-phase has an intrinsic activity equal to about 3.5 times that of the α-phase, whereas the selectivity in propene is correspondingly twice as big.

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