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THERMAL ACTIVATION OF TYPICAL OXIDATIVE DEHYDROGENATION CATALYST PRECURSORS BELONGING TO THE Ni–Mo–O SYSTEM

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$NiMoO_4$ obtained by calcination of precursors has been shown to be a very effective catalyst for oxidative dehydrogenation of propane into propene. Preparation conditions and thermal decomposition of two precursors have been studied by TG–DTA, HTXRD, FFT–IR, and thermo-desorption coupled to mass spectroscopy in order to determine their composition and to define the best treatment to favour the oxidative dehydrogenation process. The selectivity and activity for propane transformation into propene are very different depending on the nature of the precursor and of the active phases obtained after thermal activation. The more selective high-temperature β phase of $NiMoO_4$ has been obtained at a lower temperature (500°C) than previously reported (700°C).

Keywords: FFT–IR, HTXRD, Ni–Mo–O system, TG–DTA

Introduction

Increasing industrial interest in direct oxidative dehydrogenation of propane into propene has led to the development of several catalytic systems for this reaction; oxidation of propene leads to more valuable products, mainly acrolein and acrylic acid. Catalysts based on the Ni–Mo–O system have been shown to be very effective for propane transformation into propene [1], particularly stoichiometric $NiMoO_4$. This compound presents two polymorphic phases at atmospheric pressure: the low-temperature phase, α, and the high-temperature phase, β [1, 2]. The latter is more selective and, if produced at low temperature, sintering phenomena that greatly reduce its surface area, can be avoided. Some investigators [3, 4] have prepared a stable β phase at room temperature but this is a solid-solution superstoichiometric in Ni which also contains NiO. One of the aims of this investigation was to obtain a stabilized β phase without NiO.

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The active catalysts are obtained after calcination of coprecipitated precursors prepared by different routes. To date, chemical compositions of these products and their thermal evolution have not been clearly determined. In the present investigation, these catalysts have been studied by differential thermal analysis, differential thermogravimetric analysis, high-temperature X-ray diffraction, thermodesorption and fast Fourier transform infra red analysis.

Catalyst preparation

The precursor precipitation conditions are summarized below:

pH	<5.4		5.6	>6
	$\longrightarrow$			
	$\longleftarrow$			
Precipitation temperature	25°C	65°C	85°C	
	$\longrightarrow$			
Filtration temperature	25°C		85°C	
Precursor obtained	A	E	S	V

A (blue) = $(NH_4)_4H_6NiMo_6O_{24}$, mH_2O, nNH_3 (5)
E = S + A (S = stoichiometric)
S (yellow) = $NiMoO_4$, mH_2O, nNH_3
V (green) = $Ni_{1+\delta x}MoO_4$, mNH_3, nH_2O

The following equilibria exist between the different species:

$$7MoO_4^{2-}\,aq+8H^+\,aq \rightleftarrows Mo_7O_{24}^{6-}\,aq+4\,H_2O \quad (R1)$$

$$Ni^{2+}aq+MoO_4^{2-}\,aq \rightleftarrows NiMoO_4\,(s) \quad (R2)$$

$$Ni^{2+}\,aq+Mo_7O_{24}^{6-}\,aq \rightleftarrows NiMo_6O_{24}^{10-}\,aq+(Mo^{6+}) \quad (R3)$$

$$Ni^{2+}\,aq+2OH^-\,aq \rightleftarrows Ni(OH)_2\,(s) \quad (R4)$$

The general formula of these precursors is $xNiO$, $yMoO_3$, mH_2O, nNH_3 and the main reactions (Ri) are:

$$1/6 < x/y < 1 \rightarrow R2 + R3 \quad x = y \rightarrow R2 \quad 1 < x/y < \infty \rightarrow R2 + R4$$

Among these precursors, the yellow and green solids, have been particularly studied, employing a Mettler RC1 reactor calorimeter with a constant stirring speed of 100 rpm.

Yellow powder preparation

Molybdic acid 85 % (Fluka) is dissolved with ammonia (30% volume solution) in 800 ml distilled water (0.25 *M*) and heated at 85°C. The *pH* is adjusted to 5.4 and an equimolar nickel nitrate solution ($Ni(NO_3)_2 \cdot 6H_2O$, Fluka) maintained at the same temperature is added to the molybdic solution. A yellow precipitate is immediately formed and filtered after thirty minutes in thermo-regulated conditions. The precursor is abundantly washed with hot distilled water and heated for 15 hours at 120°C.

Green powder preparation

Ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, Fluka) is dissolved in 800 ml distilled water (0.25 *M*) and heated at 85°C. The *pH* is adjusted with ammonia in order to attain a NH_3/Mo ratio equal to 1.5 for this preparation. An equimolar nickel nitrate solution maintained at the same constant temperature is added to this solution with a dropping rate of 7 ml/min. A green precipitate is immediately formed, and the *pH* drops in one hour from its initial value of 8.48 to 7.09. The powder, filtered with a thermo-regulated funnel and washed with hot distilled water, is heated for 15 h at 120°C.

Experimental

X-ray diffraction patterns of products were obtained using a Siemens D5000 diffractometer with filtered CuK_α radiation. They were collected with a count time of 1 second and in the range 10–60°θ.

For high-temperature experiments an Anton Paar camera was used with a heating rate of 1 $deg \cdot sec^{-1}$ and a count time of 3 s with temperature stabilization for 60 s before pattern acquisition.

A 1700 Perkin Elmer and a Mettler TA 2000C thermal analysers were used for TG-DTA. Two types of crucible (platinum and quartz) and two different gases (nitrogen N50 or oxygen N48) were used. Samples weighed about 40 mg for platinum-crucible and 20 mg for quartz-crucible experiments. The heating rate was 20 $deg \cdot min^{-1}$ and the cooling rate 5 $deg \cdot min^{-1}$, so as to follow the natural cooling of the furnace.

A Setaram MTB-50 balance was used for thermogravimetric analysis carried out in air, with a heating rate of 5 $deg \cdot min^{-1}$. 50 mg of sample was heated in a quartz crucible.

In order to identify the desorbed gases, a few milligrams of sample were heated in a vertical furnace under vacuum and the evolved gases transported to a Balzers QMG-111-A mass spectrometer. The spectrometer measured *m/e* ratios within the range 1–200 and the heating rate used was 10 $deg \cdot min^{-1}$.

Fast Fourier transform infra red analyses were carried out on a BioRad FTS–40 instrument by diffuse reflectance on a KBr disc.

Catalytical experiments were conducted in a quartz tubular reactor on 0.5 g of catalyst mixed with a large quantity of silicon carbide granules of the same size, in order to avoid severe temperature gradients within the catalytic bed. The temperature within the catalyst layer was measured by a thermocouple placed in a thin quartz tube (diameter 2.5 mm). The gas feed was 18% O_2, 15% C_3H_8 and 67% nitrogen, at a total flow rate of 15 l/h. Before each experiment the catalyst was heated from ambient to the operating temperature under a mixture of oxygen and nitrogen (ratio O_2/N_2 = 0.7), and propane was introduced after thirty minutes.

The reactor effluents (CO_x, C_2H_4, C_3H_6, C_2H_4O and C_3H_4O) were analysed by gas chromatography; O_2, N_2 and CO by a molecular sieve 5A column connected to a thermal conductivity detector, (TCD), and ethylene, propylene, propane, and the aldehydes were separated and analysed by a porapak QS column linked first to a flame ionization detector then to a TCD.

Results and discussion

Study of the yellow powder

X-ray diffraction patterns obtained were the same as reported by Corbet [6] who identified the compound as a hydrated nickel molybdate of formula:

$$NiMoO_4, mH_2O, nNH_3.$$

When the solid sample is heated at 500°C three phenomena are observed: two endothermic peaks before 300° and an exothermic peak around 450°C. The relative weight loss is 10.6% and the gases evolved are water and ammonia. The *m/e* ratios for both compounds are given in Table 1. 5.4% of the mass, corresponding to water, is lost between 40° and 200°C and further heating to 400°C, releases ammonia (4% of the total weight) from the compound. Decomposition of the solid occurs after a sudden weight loss of 1.2% ammonia at 450°C (Fig. 1).

Table 1 Relative intensity of *m/e* ratio for water and ammonia

H_2O		NH_3	
m/e / g	Relative intensity / %	*m/e* / g	Relative intensity / %
18	100	17	100
17	21.1	16	80
10	9	13	7.5
19	5	14	2.2
20	3	18	0.4

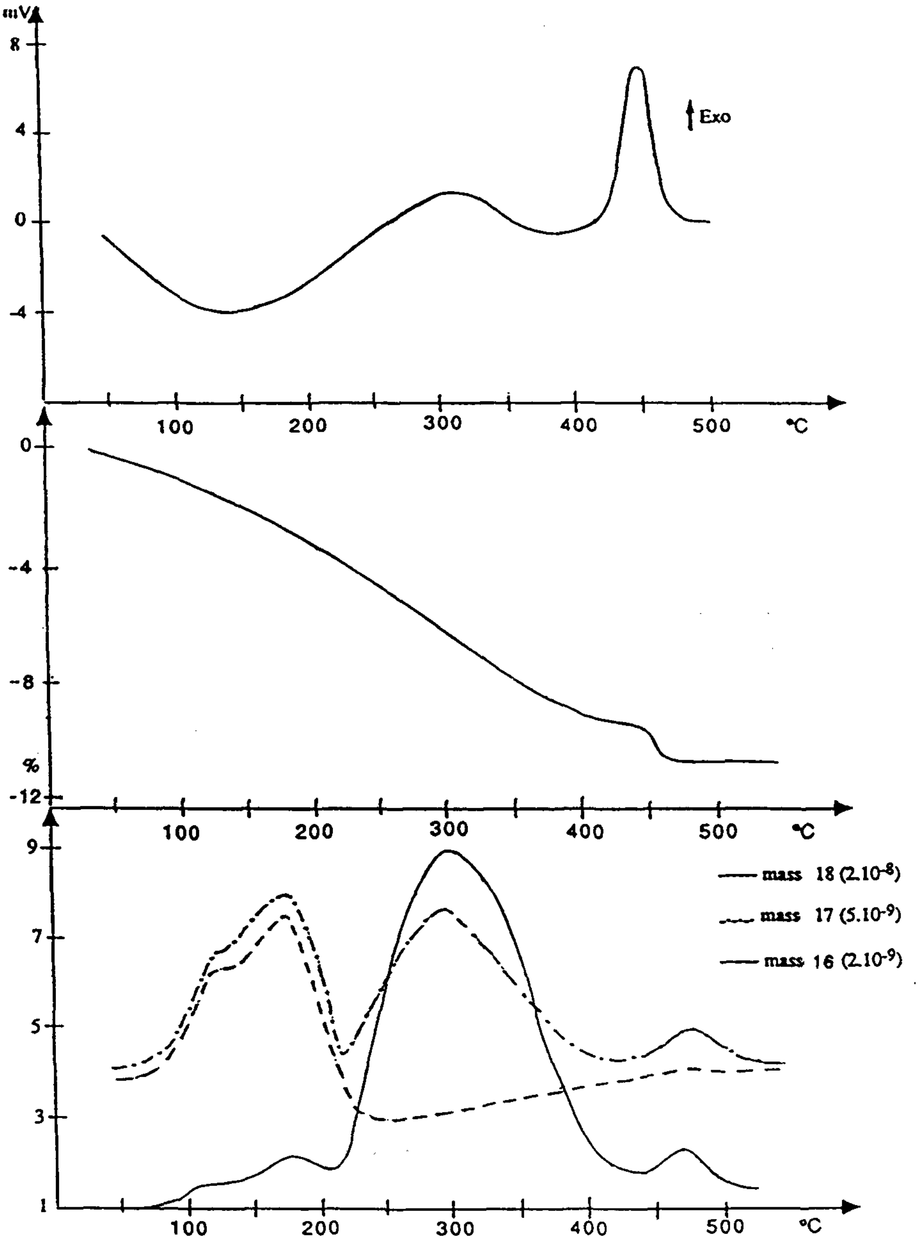

Fig. 1 Analysis of the yellow precursor

Fast Fourier transform IR analysis shows a peak at 1280 cm^{-1} representing ammonia lost during crystallization: it is present in the precursor heated at 400° but absent in the product calcined at 500°C.

High-temperature XRD reveals that the precursor structure does not change until 450°C, when it crystallizes into the high-temperature $NiMoO_4$ β phase.

The first endothermic peak is attributed to water desorption (5.4% of initial weight = 3/4 mole of water), while the second is due to loss of 7/12 mole of ammonia (4% of total weight). The final loss of ammonia (1.2% = 1/6 mole) at 450°C leads to crystallization of β $NiMoO_4$. If the Ni/Mo atomic ratio equals one, the yellow precursor formula could be:

$$NiMoO_4, 3/4H_2O, 3/4NH_3.$$

Between 700°C and 900°C a 3.7% weight loss is observed, due to sublimation of MoO_3 (endothermic peak at 780°C). Andrushkevitch [7] observed this phenomenon for precursors with Ni/Mo ratios lower than 1 and although the present solid is stoichiometric, a small amount of MoO_3 can sublimate at high temperature.

DTA and high-temperature XRD have indicated that on cooling the $\beta \rightarrow \alpha$ transition takes place at 170°C, and to obtain the β phase again it is necessary to heat the sample at 700°C [1, 2].

Decomposition of the precursor has been studied by DTA in platinum crucibles under different gaseous conditions: differences in exothermic peak intensities at 450°C depend on the gas used. If the sample is heated under oxygen, the thermal effect corresponding to this peak is twice as intense as that observed under nitrogen. This phenomenon can be explained by oxidation of NH_3 evolved from the solid according to the following reaction:

$$NH_3 + 5/4O_2 \rightarrow NO + 3/2\ H_2O$$

Three milliseconds of contact with a platinum-rhodium catalyst at 900°C is sufficient for this reaction [8]. It is exothermic ($\Delta_R G^\circ$ in $kJ\cdot mol^{-1}$= $-452.9-0.0896\ T$), but very slow at room temperature and without a catalyst. The platinum crucible probably acts as a catalyst for oxidation of ammonia at 450°C, and this has been confirmed by comparison with results obtained with quartz crucibles. Under nitrogen similar results are obtained for both types of crucible. The different thermal effects due to crystallization under oxygen and nitrogen are summarized in Table 2.

The heat of the exothermic reaction measured with a platinum crucible and in oxygen includes three calorimetric effects:

heat of ammonia desorption (endothermic effect)
heat of crystallization into β-$NiMoO_4$ (exothermic effect)
heat of oxidation of NH_3 to NO in contact with platinum (exothermic effect)

In the other cases studied, the measurement heat corresponds only to the sum of the first two contributions.

Table 2 Yellow precursor DTA results

Gas	Crucible type	Mass / mg	ΔH / $J \cdot g^{-1}$
N_2	Pt	40	–40
N_2	Quartz	20	–40
O_2	Pt	40	–120
O_2	Quartz	20	–60

When a sample calcined at 800°C is cooled, $\beta \rightarrow \alpha$ transition is observed at approximately 170°C by both DTA and high-temperature XRD. Several calcinations at 800°C (Fig. 2) have shown that the $\alpha \rightarrow \beta$ transition takes place at higher temperatures when the number of calcinations increases: it is increasingly difficult to obtain the $\alpha \rightarrow \beta$ transition in a sample which has been heated several times; the intensity of the $\beta \rightarrow \alpha$ transition peak decreases after two heating cycles. XRD analysis shows that the β phase stabilized at room temperature becomes increasingly important with each new calcination, as the partial excess of Ni in the solid due to sublimation of small quantities of MoO_3 at each cycle has a stabilizing effect on β-$NiMoO_4$ [4].

Study of the green powder

X-ray diffraction patterns observed by Astier [9] match exactly the one obtained for the green product. DTA (platinum crucible, nitrogen) shows one large endothermic peak at 410°C. This corresponds to a weight loss of 13.75% and no further loss in observed after 500°C. Only two gases are detected by thermodesorption: water and a large amount of ammonia, probably in the ratio 1:5 (Fig. 3).

By FFT-IR analysis a large amount of ammonia is observed (peaks at 1400 and 3200 cm^{-1} corresponding to NH_4^+ cations). The peak at 1280 cm^{-1} (NH_4^+) represents the amount of ammonia lost during crystallization. The marked presence of NH_4^+ cations in the precursor structure is accompanied by a large amount of hydroxyl group (peak at 1620 cm^{-1}).

When all the water and ammonia are evolved, β $NiMoO_4$ is obtained, as confirmed by high-temperature XRD. To a first approximation, if the Ni/Mo ratio is assumed to be almost equal to one and the NH_3/H_2O ratio to be 5, the formula of green precursor could be:

$$Ni_{1+\delta x}MoO_4,\ 5/3NH_3,\ 1/3H_2O$$

Astier [9] has proposed a Ni/Mo ratio equal to 0.8 for this precursor, which is not justified on the basis of FFT-IR and XRD. The results did not reveal the presence of MoO_3 in excess after thermal decomposition.

When cooling this product at 5 deg·min^{-1}, an exothermic peak corresponding to the $\beta \rightarrow \alpha$ transformation is observed around 170°C. When studying the sample

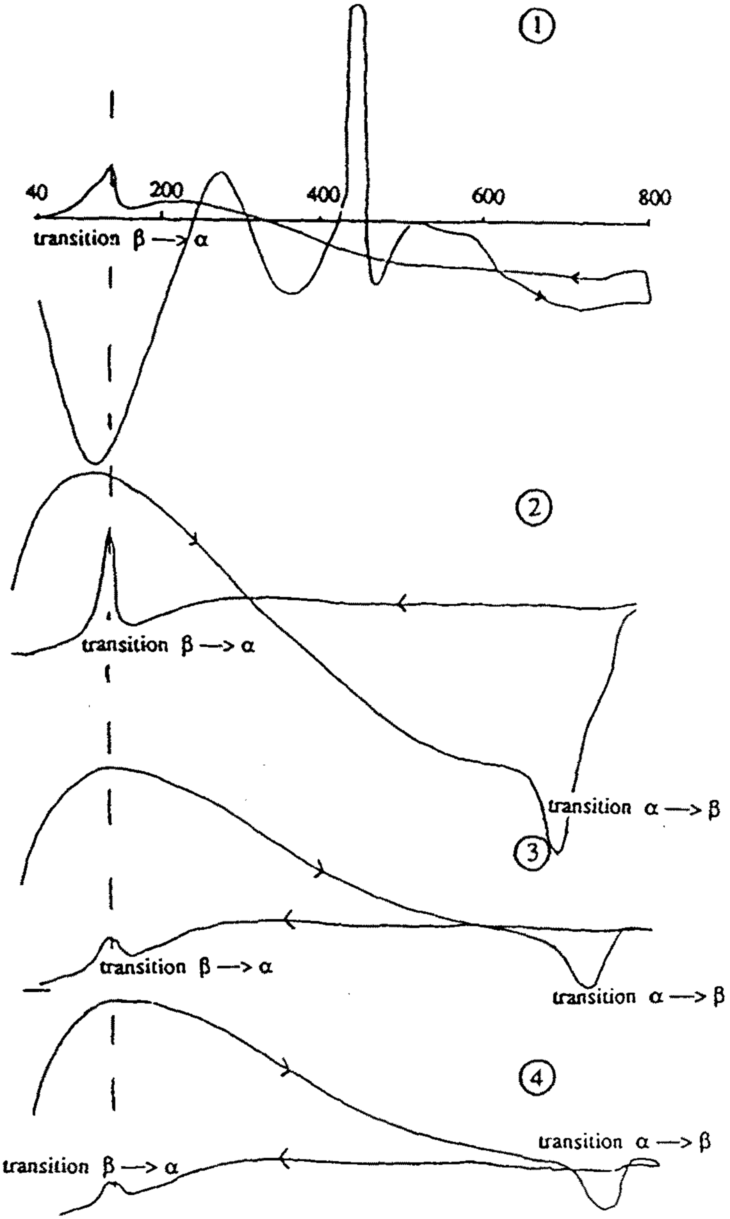

Fig. 2 DTA cycles of yellow precursor calcination (gas: N_2, crucible: Pt)

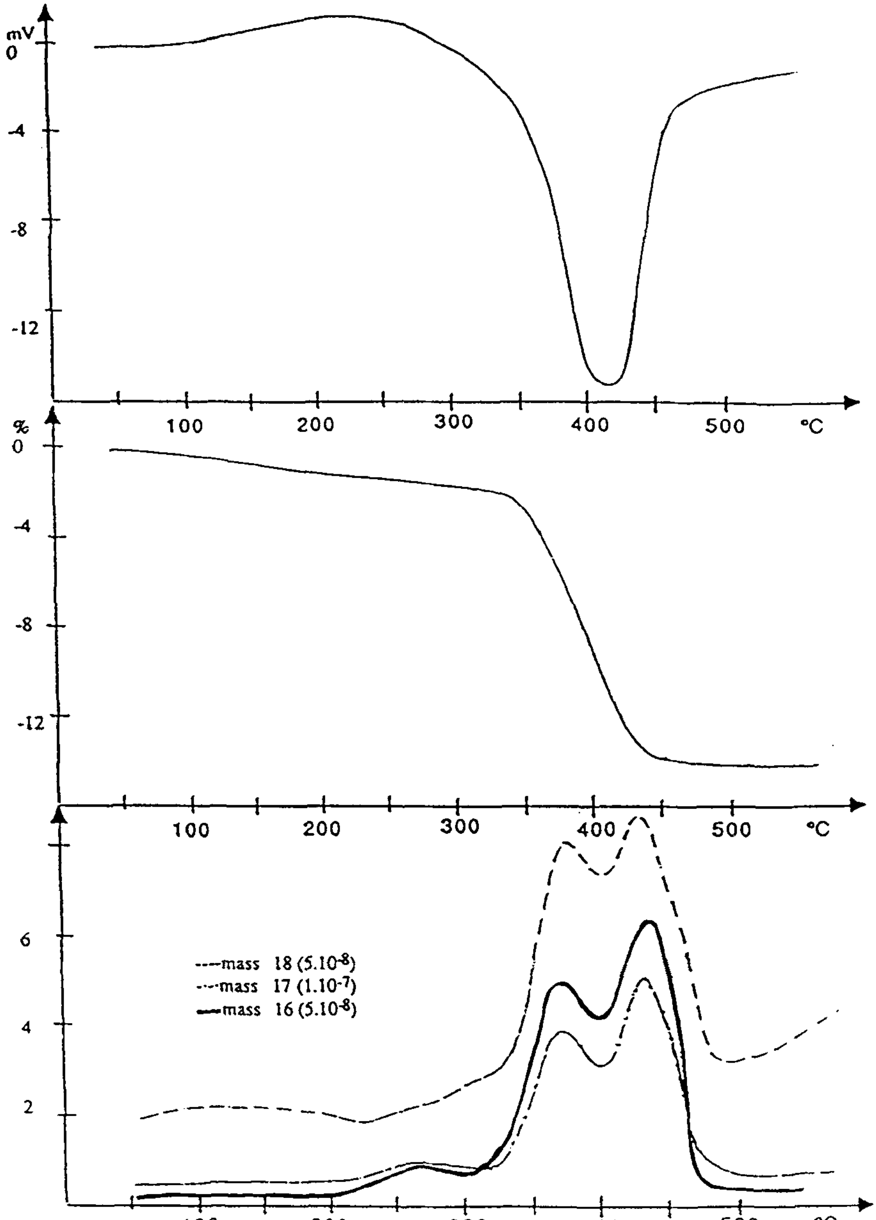

Fig. 3 Analysis of the green precursor

by high-temperature XRD, the β →α transition is not immediatly observed probably because the cooling rate is different. The sample must remain for half an hour at room temperature to be partially transformed into the α phase. It can be concluded therefore that the α-$NiMoO_4$ phase needs a finite time to crystallize at room temperature. A similar phenomenon was observed by Trambouze and Colleuille [10] for $CoMoO_4$.

Calcination to 500°C of the green precursor has been studied by DTA. With nitrogen, an endothermic peak is observed around 400°C, and an exothermic peak is observed at the same temperature with oxygen. The conclusion is the same as for the yellow precursor: the desorbed ammonia reacts with oxygen to give NO in contact with platinum (Table 3).

Table 3 Green precursor DTA results

Gas	Crucible type	Mass / mg	ΔH / J·g^{-1}
N_2	Pt	40	325
N_2	Quartz	20	300
O_2	Pt	15	-500
O_2	Quartz	10	425

When several consecutive calcinations of the same sample are studied, by DTA, the α → β transition always takes place at the same temperature, whereas the β → α transition occurs on cooling progressively at lower temperatures (Fig. 4). The area of the DTA peak of the β → α transition decreases and the amount of β phase stabilized at the end of each cycle increases with number of calcinations.

Comparison of the two products and catalytic properties

Stabilization of the β phase obtained by calcination of the green precursor is probably due to the presence of nickel in slight excess. This conclusion is supported by XRD and FFT-IR experiments. The ratio of the principal XRD lines for both phases changes and an increase in β with respect to α is observed (β/α molar ratio is negligible for the yellow precursor and equal to 0.13 for the green one). IR analysis confirms the presence of the stabilized β phase (bands at 810 and 880 cm^{-1}) [1].

XRD analysis after each calcination to 800°C for the two products provides evidence of stabilization of the β phase with number of calcinations. This stabilization is already evident for the green powder after the first heating cycle. For the yellow powder this phenomenon appears after the third cycle, as it is due only to the smaller Ni excess deriving from sublimation of MoO_3 (Fig. 5).

The catalytic behaviour of the β and α phases prepared from yellow or green precursors are compared in Table 4, in particular catalytic properties of the β

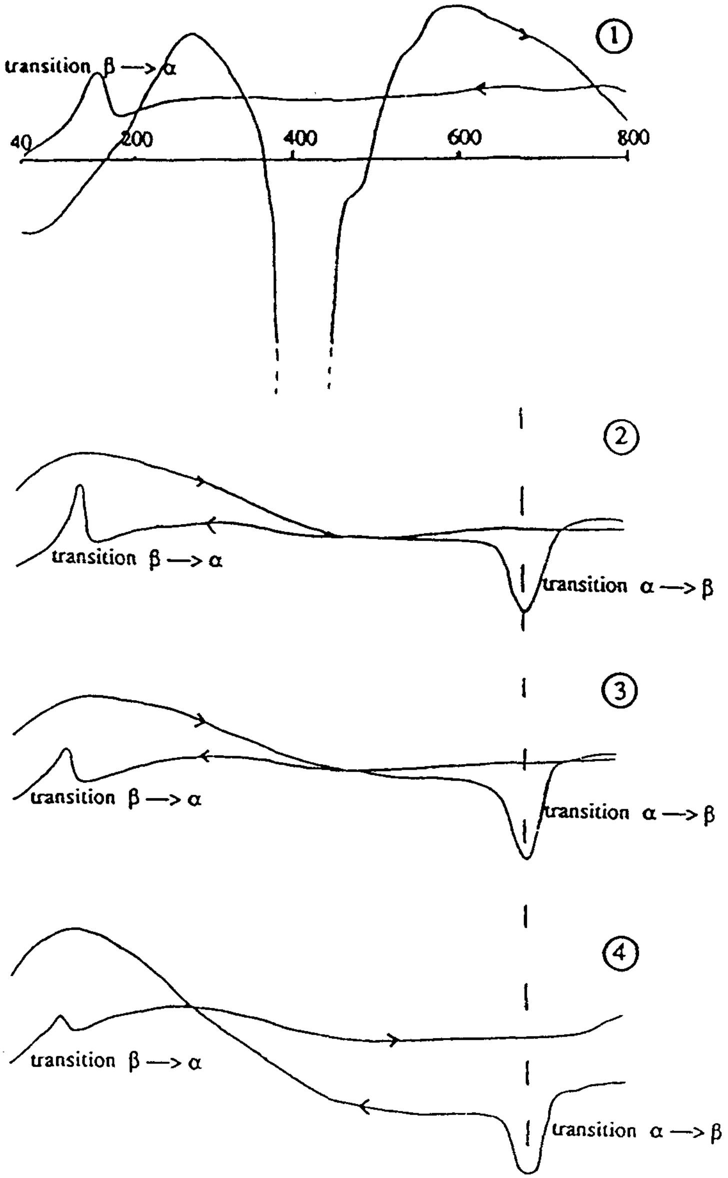

Fig. 4 DTA cycles of green precursor calcination (gas:N_2, crucible: Pt)

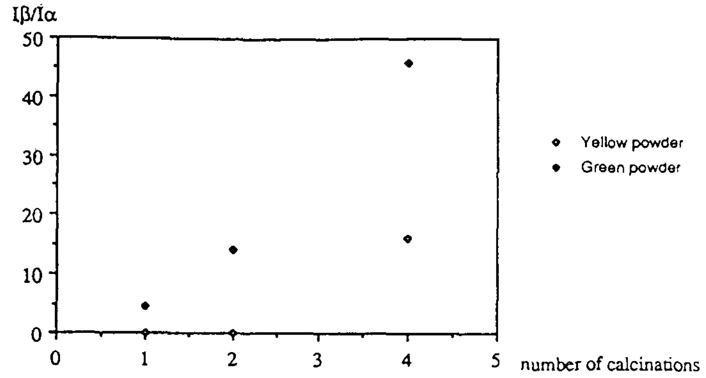

Fig. 5 Ratio of the intensities of the main lines of the β- and α-NiMoO$_4$ phases

phase obtained 'in situ' and the α phase obtained after a conventional thermal treatment (precursor heated to 550°C for 2 h then cooled at room temperature). The catalysts obtained from the yellow precursor show the best results for conversion of propane. The α phase is more active but less selective.

A yellow precursor calcined 'in situ' in the reactor (β phase at 500°C) shows a propene selectivity almost as great as that of the yellow catalyst obtained by heating the α phase from 25° to 700°C, maintaining it at this temperature for ten minutes and cooling at the reactor temperature (Table 5); however, the former product has a much better propane conversion (18.3 against 10%)

Table 4 Conversion of propane in %

	500°C	530°C
Yellow precursor calcined in situ	10.2	18.6
Green precursor calcined in situ	6.3	6.9
Yellow precursor calcined before	14.6	24.4
Green precursor calcined before	7	7.9

Table 5 Conversion of propane and selectivity for catalyst prepared from yellow precursor

Catalyst	Temperature /°C	Propane conversion /%	Propene selectivity /%
α-NiMoO$_4$[1]	530	24.4	42.8
High-temperature β-NiMoO$_4$ phase[2]	530	10	78.5
Low-temperature β-NiMoO$_4$ phase[2]	530	18.3	65.7

[1] Heated at 550°C, cooled at room temperature, heated at 530°C; 'classical α'

[2] Heated at 700°C for ten minutes; 'classical β'

[3] Heated at 550°C for two hours: 'β in situ'

Conclusions

Coprecipitation from an ammonia solution leads to two different precursors, yellow or green, which have different formule, thermal behaviour and catalytic properties. The phase crystallizing after thermal decomposition is β-$NiMoO_4$. When a yellow precursor is calcined 'in situ' better catalytic results are obtained in the propane-propene conversion.

* * *

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Zusammenfassung — Durch Kalzinierung von Präkursoren hergestelltes $NiMoO_4$ erwies sich als sehr wirkungsvoller Katalysator für die oxidative Dehydrogenisierung von Propan zu Propen. Mittels TG-DTA, HTXRD, FFT-IR und Thermodesorption/MS wurden die Herstellungsbedingungen und die thermische Zersetzung von zwei Präkursoren untersucht, um ihre Zusammensetzung zu ermitteln und um die beste Art zur Begünstigung des oxidativen Dehydrogenisierungsprozesses zu finden. Selektivität und Aktivität der Umwandlung von Propan zu Propen ist je nach Art des Präkursors und der nach thermischem Aktivieren erhaltenen aktiven Phasen sehr verschieden. Die selektivere Hochtemperatur β-Phase von $NiMoO_4$ wurde bei einer niedrigeren Temperatur (500°C) erhalten, als bis dahin beschrieben (700°C).