EFFECTS OF THERMAL TREATMENTS ON A NiMoO$_4$ PRECURSOR PREPARED BY IMMOBILIZING Ni$_{aq}^{2+}$ AND MoO$_{4aq}^{2-}$ IN AN ORGANIC MATRIX

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Abstract

A novel preparation methodology of NiMoO$_4$ catalysts is described, consisting in immobilizing a precursor aqueous solution containing Ni and Mo ions by gelation with agar. Compared with other precursors prepared by coprecipitation, the gel, on heating, begins to crystallize at a very low temperature, with the collapse of the gel structure.

The elimination of the water representing the greatest part of the gel weight is the predominant phenomenon taking place during the thermal activation treatment and the phase composition of the oxide formed changes as follows: fast heating favours the stabilization at room temperature of the metastable tetrahedral β-NiMoO$_4$ phase, while slow heating allows an increased formation of the more stable octahedral α-phase.

Keywords: Ni–Mo–O system, oxidative dehydrogenation, preparation methodology, propane

Introduction

NiMoO$_4$ catalysts have shown a remarkable activity in the partial oxidation of several paraffinic and olefinic hydrocarbons [1, 2]; both the low temperature α-phase and the high temperature β-phase are catalytically active. For C$_3$ conversion, and particularly in the case of oxidative dehydrogenation of propane, the β-NiMoO$_4$ phase leads to the highest propene yields [3].

The catalyst precursor is commonly prepared by coprecipitation in an aqueous ammonia solution. By carefully controlling the precipitation conditions (temperature, *pH*, time, filtration temperature) it is possible to precipitate a partially crystalline yellow powder (I), whose X-ray diffraction pattern corresponds to the formula NiMoO$_4$, mH$_2$O, nNH$_3$ [4]. Upon heating, the high-temperature β-NiMoO$_4$ phase crystallizes at 470°C, and on cooling, it transforms into the low-temperature α-NiMoO$_4$ phase around 150°C; α-NiMoO$_4$ is stable up to 600°C [5]. At higher temperatures the α → β phase transition starts and a few minutes at 700°C are enough to obtain only, the pure β-phase [6]. β-NiMoO$_4$ is used as a catalyst in the temperature range 200–650°C.

It has been shown that it is possible to prepare these catalytically active $NiMoO_4$ phases also starting from organic compounds. A precursor composed of mixed Mo and Ni oxalates (Ni:Mo = 1:1) has been prepared by coprecipitation and, differently from the case of (I), after thermal activation it was possible to observe the presence of both $NiMoO_4$ phases at room temperature [7]. High-temperature XRD studies had previously indicated that incorporation of a small excess of nickel ions could alter the β-$NiMoO_4$ tetrahedral configuration, due to the formation of a solid solution which remained stable at room temperature, not allowing the $\beta \rightarrow \alpha$ phase transition to occur [8, 9].

Another way to prepare the $NiMoO_4$ catalytic system is by using natural substances or polymers in order to create a polymeric network, containing the ionic components of the active catalyst trapped inside the organic matrix [10]. In the present work a novel preparation methodology of $NiMoO_4$ is reported, in which the precursor is an organic gel (agar) containing Ni and Mo ions (Ni:Mo = 1:1 atomic ratio). This methodology offers several advantages: it is cheap, and multicomponent catalytic systems can be prepared by simply dissolving in the aqueous solution the proper concentration of the desired elements. A $NiMoO_4$ catalyst prepared from the gel has been tested in the oxidative dehydrogenation of propane to propene, and the results were compared with those obtained with the standard catalyst (I) prepared by coprecipitation.

Experimental

Gel preparation

Equimolar aqueous solutions (0.5 molar) of nickel nitrate hexahydrate and ammonium heptamolybdate tetrahydrate (FLUKA reagents) are mixed at ambient temperature under continuous stirring. 1% (w/w) agar powder (SIGMA) is added and the solution is heated at a temperature of 80°C in order to solubilize the agar. A rapid cooling of the solution leads to the formation of the gel that can be kept at low temperature or freeze-dried to maintain its stability.

Catalyst preparation

The gel was slowly dried by heating from room temperature up to 120°C (heating rate of $10°C\ h^{-1}$) to eliminate water, and then maintained for 4 h at 120°C. Several catalysts were prepared by applying different thermal activation treatments to the dried powder: some were introduced in the pre-heated oven and kept for 12 h at the chosen temperatures (250, 350, 450 and 550°C), while others were slowly heated up to the same temperature ($1°C\ min^{-1}$) and kept there for twelve hours before cooling.

Physico-chemical characterization

The presence of crystallized α- and β-NiMoO$_4$ phases in the samples undergoing the thermal treatments described above was studied by XRD. The diffraction patterns were taken at room temperature, using a Philips mod. PW 1710 BASED diffractometer with filtered CuK$_α$, radiation.

The same samples have also been characterized by FT-IR (Perkin Elmer Mod.1760, KBr disks). This analysis revealed the presence of NiMoO$_4$ phases and of residual ammonium and nitrates, originally present in the starting Ni and Mo salts.

Thermal studies of the decomposition of the precursors were performed on a Mettler TA 2000C instrument. Samples weighing about 20 mg were placed in platinum crucibles, then heated at 10 or 20°C min^{-1}, while recording the DTA, TG and DTG curves. The tests have been conducted in both oxidative (air) and inert (nitrogen) atmospheres (Gas Feed = 6 l h^{-1}).

Catalytic runs

The catalysts obtained by heating the dried gel directly at 550°C for twelve hours have been tested for oxidative dehydrogenation of propane. 0.5 g of catalyst was placed inside a tubular quartz reactor (i.d. = 1 cm) after mixing with a large quantity of silicon carbide granules of the same particle size, in order to avoid severe temperature gradients within the catalyst bed. The gas feed was composed of 18% oxygen, 15% propane and 67% nitrogen, with a total flow rate of 15 l h^{-1}. Propane was introduced at 500°C after one hour stabilization of the reactor. Once the reactor had attained the stationary conditions, which required a couple of hours, on-line sampling was performed at regular time intervals (every hour). The reaction products were analysed by gas chromatography (TCD and FID).

Results and discussion

a) Activation of the precursor

In Fig. 1 the mass losses observed for the dried and the wet gel samples on heating in air are demonstrated. It can be seen that the drying treatment almost completely eliminates water, which represents more than 90% of the fresh gel mass. The total mass loss of the dried gel treated in oxygen and nitrogen is 13.3 and 12.5%, respectively. Comparison of the two TG curves suggests an insignificant influence of the gaseous environment on the decomposition, as shown in Fig. 2 where the differential mass loss curves (mass loss /total mass loss%) are indicated for the two cases.

XRD analysis (Fig. 3) indicated that the dried gel is already a partially crystallized compound, and several lines belonging to both the α- and β-NiMoO$_4$ phases can be detected [11].
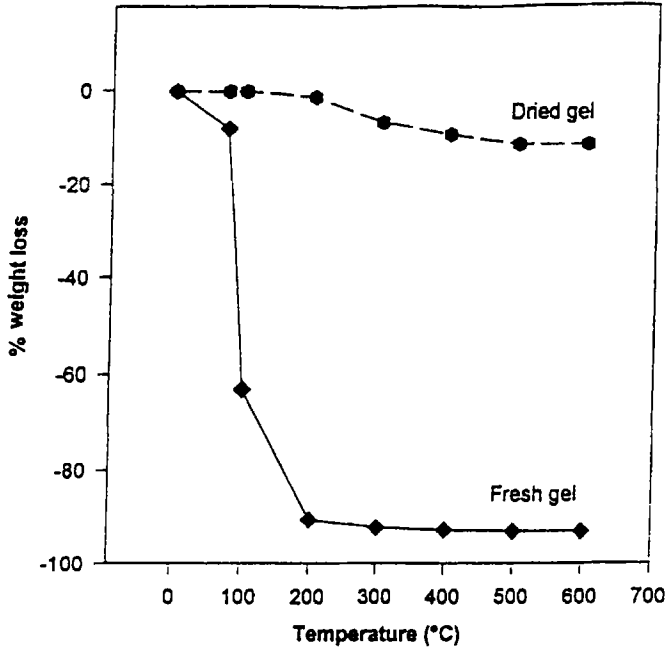
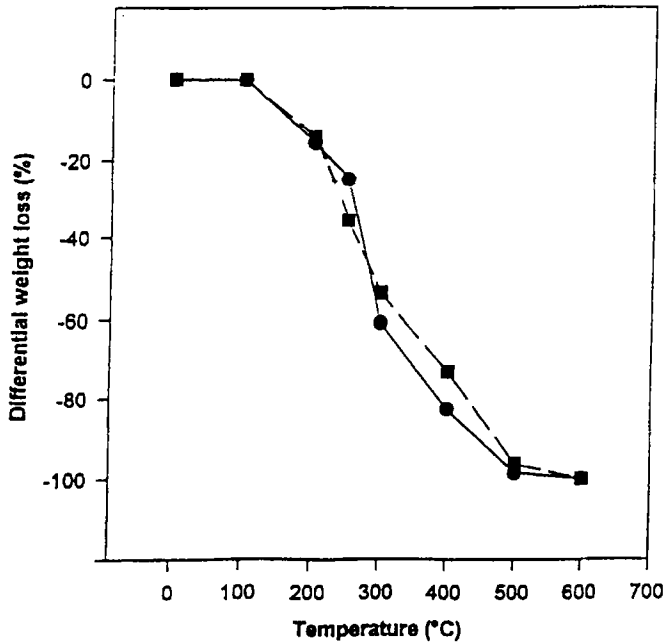Fig. 1 Mass loss of dried (a) and non-dried (b) gel samples

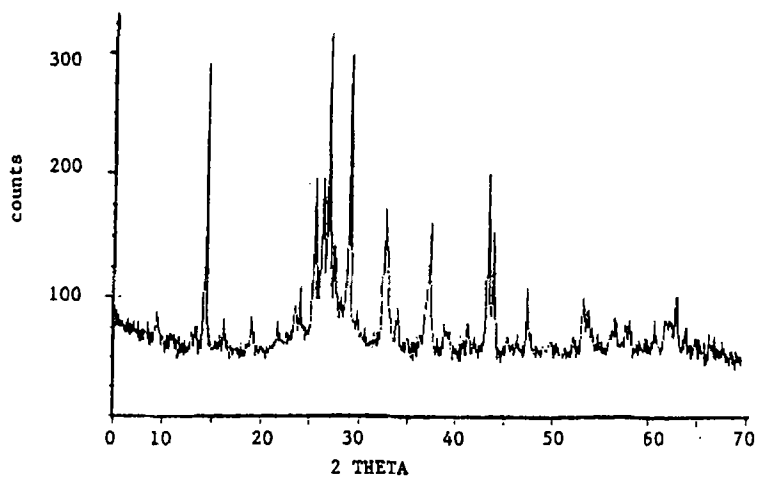Fig. 2 Differential mass loss of the gel in air (•) and nitrogen (■)

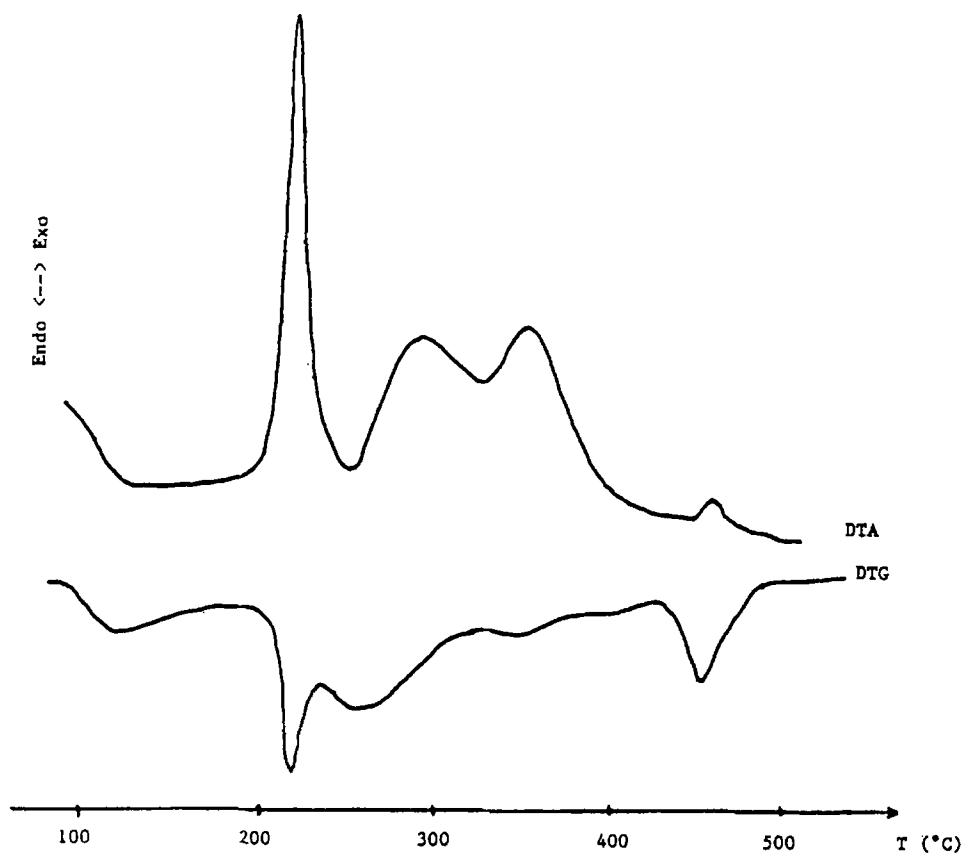**Fig. 3** X-ray diffraction pattern of the dried gel

Fig. 4 DTA and DTG curves of the dried gel in air

In Figs 4 and 5 the thermal curves of the dried gel recorded in air and nitrogen up to 600°C are illustrated. Several phenomena can be observed:

– the main exothermic effect occurs above 200°C both in air and nitrogen atmosphere. Corresponding to this exothermic effect an abrupt acceleration of the mass loss can be observed in the DTG curves. The fast elimination of volatile compounds contained in the precursor matrix has often been observed to accompany the crystallization of the oxide systems [12], and this could indicate a further $NiMoO_4$ crystallization;

– between 300 and 400°C an exothermic reaction is observed, particularly in air. In this range both the nitrates and ammonia are eliminated, and the agar decomposes to carbon oxides in the presence of oxygen. It was previously shown that the elimination of ammonia becomes oxidative when using Pt crucibles in the presence of oxygen [5], and this together with the formation of carbon oxides explains the exothermic effects observed in air;

– at 470°C, in air and oxygen, a small exothermic DTA peak and a DTG peak can be noticed. This can be attributed to a final crystallization, since it has been observed that the crystallization of $NiMoO_4$ from the precursor (I) starts at the same temperature [5].
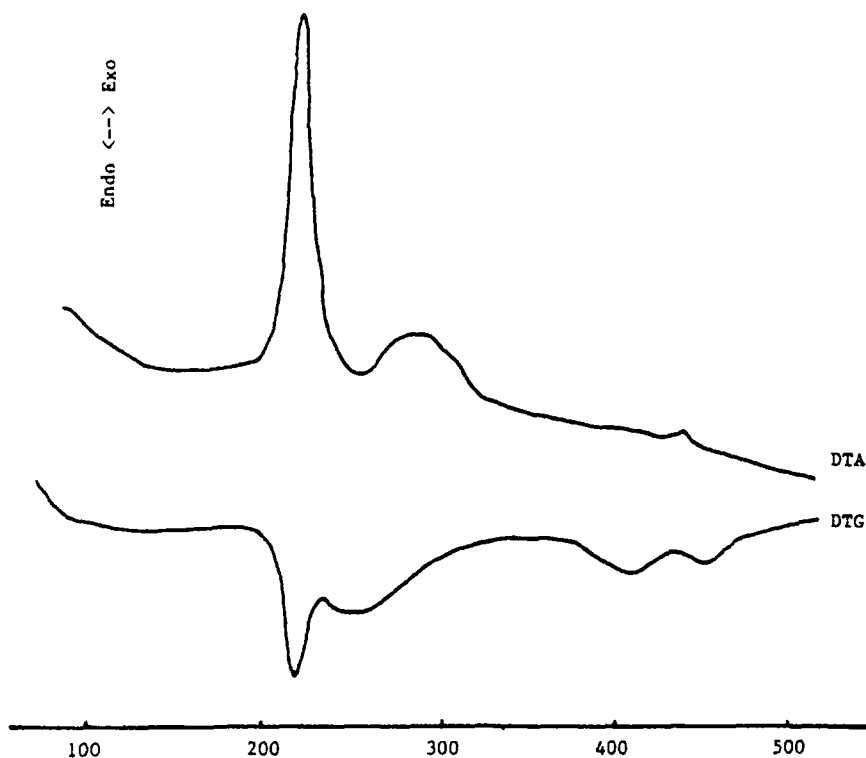

Fig. 5 DTA and DTG curves of the dried gel in nitrogen

This finding is confirmed by FT-IR experiments: nitrates and ammonia disappear only when the sample is treated at high temperature, while the peaks of α and β nickel molybdate are better resolved (Fig. 6).

XRD analysis performed at room temperature on samples heated at different temperatures indicate that already at a temperature of 350°C only the α- and
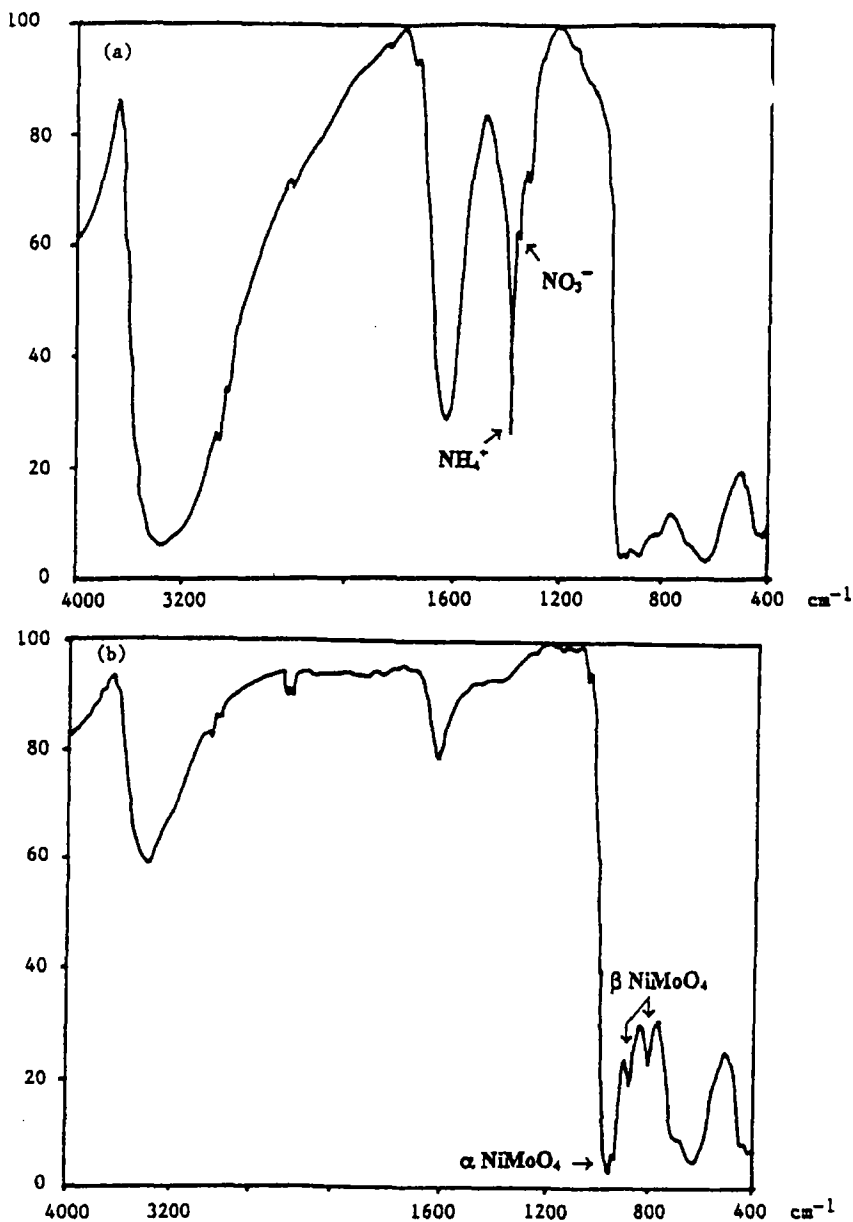

Fig. 6 Infrared analysis of the gel heated at 250°C (a) and 550°C (b)

β-NiMoO₄ phases are present. MoO₃ and NiO lines are absent in all the examined samples, confirming that the homogeneous dispersion of Ni and Mo ions in the precursor leads specifically to the formation of NiMoO₄ phases.

The experimental procedure used for activating the precursor influences the ratio between the α- and the β-phases. Direct heating always leads to the predominance of the β-phase when 350≤T≤550°C (Figs 7b, 8b), while when the dried sample is gradually heated, the α-phase prevails already at 350°C (7a). Further heating at 550°C for 2 h causes a reduction in the number and intensity of the lines of the β-phase (Fig. 8a).

The stabilization of the β-phase at room temperature observed in the case of the samples obtained by direct heating can be explained [7] by the formation of a solid solution between the β-phase and a small excess of available Ni ions.
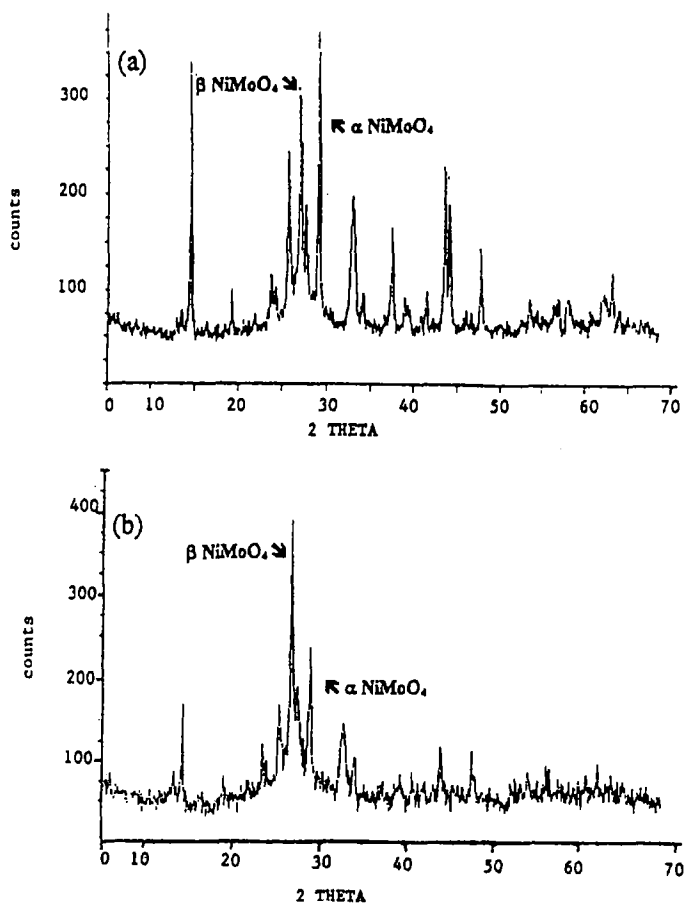

Fig. 7 XRD spectra of gel samples heated at 350°C; a) heating rate 1°C min⁻¹, b) introduced directly in the oven at 350°C
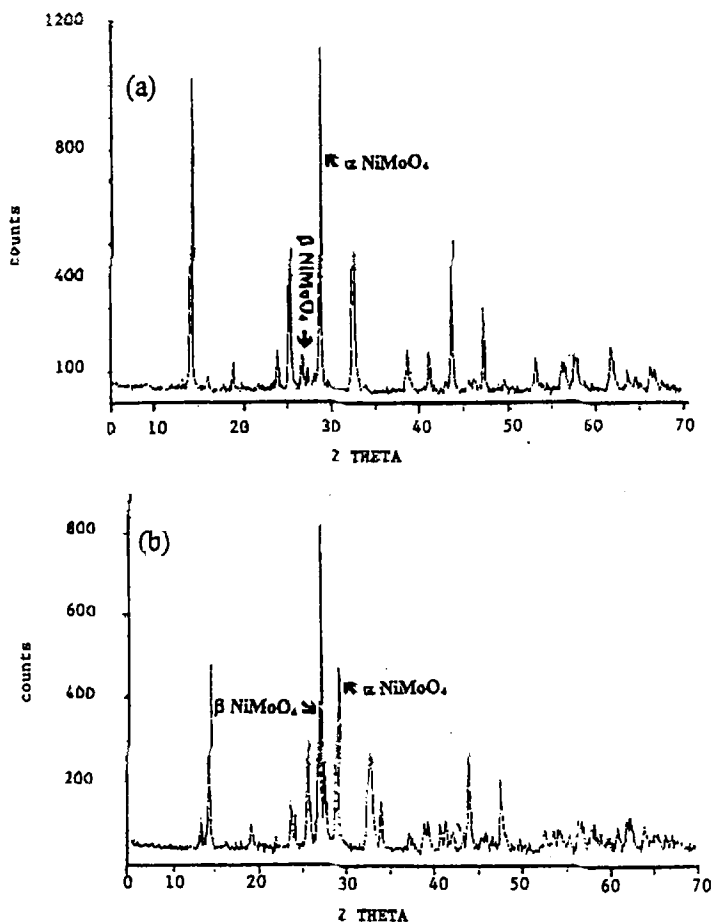
Fig. 8 XRD spectra of gel samples heated at 550°C; a) heating rate 1°C min^{-1}, b) introduced directly in the oven at 550°C

This availability is reduced when the crystallization occurs more slowly (samples gradually heated). In the latter case the high-temperature β-phase is more easily transformed into the α-phase on cooling.

b) Catalytic tests

The NiMoO$_4$ catalysts used for catalytic tests on the oxidative dehydrogenation of propane contained mainly the β-phase as measured by XRD (Fig. 7b).

The results of catalytic tests are listed in Table 1 together with those obtained with pure α- and β-NiMoO$_4$ phases (I) under the same experimental conditions.

Table 1 Catalytic results of NiMoO₄ catalyst obtained from the gel and by coprecipitation

Catalyst	$T/^{\circ}C$	%Conv.	CO	CO_2	C_2H_4	C_3H_6	C_2H_2O	C_3H_4O	Propene productivity/mmol h⁻¹
						%Selectivity			
[1]α + β NiMoO₄	450	3.1	0.20	17.6	0.0	80.8	0.0	1.4	1.4
[1]α + β NiMoO₄	475	3.8	0.30	18.7	0.0	78.7	0.0	2.3	1.7
[1]α + β NiMoO₄	500	4.4	0.40	19.4	0.0	77.4	0.0	2.8	1.9
[2]α NiMoO₄	500	9.6	23.0	21.4	0.6	49.0	0.6	4.0	4.7
[2]β NiMoO₄	500	7.2	10.3	8.0	0.3	78.1	0.3	2.5	2.5

Feed: 15% C₃H₈, 18% O₂ the rest N₂; total feed 15 l h⁻¹

[1]α/β phase ratio=0.5 (ratio between the intensity of the principal line of the specific phase in the mixture and the intensity of the principal line of the pure phase)

[2]standard catalyst prepared by coprecipitation

The catalysts obtained starting from the gel showed a propene selectivity similar to the one observed with the pure β-phase, but a poorer propane conversion even in the presence of the more active α-phase. No difference can be noticed relative to acrolein selectivity, while differently from (I), CO_2 and almost no CO is formed. This may be due to a strong propene adsorption which leads to its total oxidation, as confirmed by the absence of partial oxidation products (ethylene and acetaldehyde).

Conclusions

The immobilization of Ni and Mo inorganic ions dissolved in water inside agar gel allows a partial crystallization of the $NiMoO_4$ oxide system. Depending on the thermal treatment various α/β $NiMoO_4$ phase ratios can be obtained.

This simple preparation procedure is particularly interesting in view of the possibility of varying the Ni/Mo ratios with the simultaneous presence of the promoters.

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