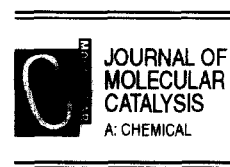




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Oxidative dehydrogenation of butane: changes in chemical, structural and catalytic behavior of Cs-doped nickel molybdate

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Abstract

The effect of doping NiMoO₄ with increasing Cs concentrations (1, 3 and 6%), on the crystalline structure, chemical nature and catalytic behaviour for the oxidative dehydrogenation of butane, was studied. The atomic ratio Mo/Ni = 1 and the cesium concentration were checked by several techniques (X-ray photoelectron spectroscopy, atomic absorption, inductively coupled plasma spectroscopy). The structural study of the α - and β -phases was carried out by high temperature X-ray diffraction and showed that Cs does not affect the molybdate structure at room temperature. However it makes the transition from α - to β -phase by heating difficult. Cs remains on the catalyst surface blocking pores and reducing BET surface area. The acid and basic natures of the catalysts were studied by NH₃ and CO₂ temperature programmed desorption, respectively. The formation of nitrogenated compounds during the NH₃-TPD was observed. CO₂-TPD shows an increase in the catalyst basicity with Cs doping, but overdoping was observed for the 6% Cs–NiMoO₄ catalyst. The catalytic tests showed a decrease of activity with the Cs content. In both the α - and β -phases the selectivity to dehydrogenation products increases with the Cs contents, but tends to decrease for the 6% Cs–NiMoO₄, due to the overdoping effect. This effect in the α -phase and the β -phase stabilisation in the catalyst with higher Cs contents, contributes to an increase of the activity normalised to surface area.

Keywords: Oxidation; Dehydrogenation; Nickel molybdates; Butane; Promoters

1. Introduction

It is well known that NiMoO₄ may have three different structures, but, only two of them are stable at atmospheric pressure [1]. NiMoO₄

shows a octahedral coordination of Mo (α -phase) at room temperature. It is stabilised in tetrahedral coordination (β -phase) at high temperature and cannot be quenched to ambient temperature.

The catalytic activity of both phases was studied by several researchers. However, while Itenberg [2] found that both phases present similar activity and selectivity in the oxidative dehydrogenation of n-butane into butadiene, it is generally accepted [1,3] that the α -phase is more

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active and the β -phase is more selective for this kind of alkane reactions. New preparation methods using organic salts have recently been tested in order to induce a greater stabilization of β -phase at room temperature [4] for obtaining better selectivities and to avoid the continuous heating required to maintain the catalyst in its β -configuration.

The catalytic behaviour of the NiMoO_4 is not only influenced by the crystalline structure. The chemical nature of catalyst surface (acidity/basicity) also influences the activity and product distribution with oxide-based catalysts [5,6]. On the other hand, alkali metals used as promoters also affect the activity and selectivity of the catalyst according to the nature of the promoter ion [3,7]. No papers were found concerning the effect of alkaline cations on physicochemical properties of the Ni–Mo–O system. However, a few papers studied these aspects for other catalytic systems, such as $\text{V}_2\text{O}_5\text{--TiO}_2$ [8,9] or $\text{MoO}_3\text{--TiO}_2$ [10–12], including active ones for the dehydrogenation of alkanes [13].

It is therefore of great interest to study the structural and chemical aspects of NiMoO_4 not yet clarified, the changes that the cesium deposition causes in them, as well as the relationship between the chemical and physical properties and the activity/selectivity of these catalysts for the oxidative dehydrogenation of butane.

2. Experimental

An unsupported $\alpha\text{-NiMoO}_4$ catalyst was prepared by coprecipitation reaction according the method described by Mazzocchia et al. [14] with a Mo/Ni atomic ratio of 1. Cesium doped catalysts were prepared by wet impregnation of the $\alpha\text{-NiMoO}_4$ over about 15 h at 60°C , using cesium nitrate; the liquid to solid ratio was 10 by weight. The impregnated sample was filtered and dried at 120°C for 4 h and finally calcined in air for 2 h at 550°C .

The characterization of the prepared catalysts was carried out by Inductively Coupled Plasma Spectroscopy (ICP), Atomic Absorption (AA), XRD, IR and XPS. Experimental details can be found elsewhere [3]. All the catalysts had an atomic ratio Mo/Ni = 1 and a cesium surface concentration of 1, 3 and 6%.

The surface areas of all catalysts were determined by the nitrogen BET method. An attempt was made to estimate the surface areas of β -phase catalysts by quenching them after the thermal treatment required to produce the β -phase, although this phase cannot be completely stabilized at room temperature as shown by the XRD experiments.

The structural study of both α - and β -phases was carried out by XRD in a Rigaku apparatus using the $\text{Cu K}\alpha$ radiation (Ni filter) from 10 to 50° , at $2^\circ/\text{min}$. The spectra were recorded at 21°C for the α -phase. The activation to β -phase was made in situ with air flow, heating the sample at $20^\circ\text{C}/\text{min}$ up to 710°C and maintaining this temperature for 10 min before recording the spectrum [1].

The acidity/basicity of the catalyst's surface was studied by NH_3 and CO_2 TPD, respectively. The NH_3 -TPD experiments were performed only for some samples adsorbing NH_3 at 30°C because formation of nitrogenated compounds was observed. The CO_2 -TPD experiments were carried out adsorbing CO_2 at 30 and 250°C . The catalyst was pretreated by heating the sample in He flow up to 550°C to clean the surface, but avoiding the transition to β -phase. One previous experiment carried out in He flow up to 650°C showed that between 550 and 650°C the detector signal is negligible. In both cases about 0.3 g of the catalysts were saturated in NH_3 or CO_2 at the corresponding temperature and then desorbed by heating at $10^\circ\text{C}/\text{min}$ in a He flow of $1\text{ cm}^3/\text{s}$, with on-line gas analysis performed with the TC detector of a Shimadzu GC-8A gas chromatograph.

The catalytic experiments were carried out in a fixed-bed, continuous flow tubular quartz reactor (I.D. 20 mm; length 600 mm) with a

coaxially centered thermocouple. The catalyst charge was 0.3 g mixed with quartz in a volume ratio of 1:2 catalyst to quartz. This catalyst charge was chosen for always having differential conversions. All the experiments were performed at atmospheric pressure. The feed was a mixture of butane, oxygen and nitrogen with molar ratio of 4/9/87 and the contact time was equivalent to $W/F = 12 \text{ g} \cdot \text{h}/\text{mol}_{\text{butane}}$. The catalytic tests were performed between 375 and 575°C for α -phase and 425–600°C for β -phase. The β -phase catalysts were formed in situ by heating α -phase catalysts at 710°C in air flow for 10 min, and then cooling to the predetermined temperature. The stability of the β -phase was checked throughout the temperature range used.

Blank runs proved that under the experimental conditions used the homogeneous reactions can be neglected.

Analyses of reactants and products were carried out by an on-line Shimadzu GC-8A gas chromatograph with two columns: (i) molecular sieve 13X (60–80 mesh, 2 m \times 1/8 in. stainless steel); (ii) 33% dimethylsulpholane on Chromosorb P (60–80 mesh, 6 m \times 1/8 in.).

3. Results and discussion

3.1. Catalyst characterization

AA, ICP and XPS measurements confirmed an atomic ratio $\text{Mo}/\text{Ni} = 1$ (stoichiometric NiMoO_4) and only traces of alkali metal were detected in the bulk of the catalysts. XPS evidenced that the surface cesium concentration is in agreement with the expected dopage: 1, 3 and 6% (Table 1). In addition, the binding energies of Mo_{3d} XPS spectra becomes lower in the doped catalysts, which suggests an increase of the average electron density [3].

The unpromoted NiMoO_4 and the Cs doped catalysts were structurally studied at room temperature (21°C) by XRD (Fig. 1). The α -molybdate showed only the peaks of the α -phase (ASTM – 33-948). The results show that doping with Cs does not produce apparent changes in the molybdate structure, independently of the alkali concentration. Cs remains only on the catalyst surface and does not produce segregation of NiO or MoO_3 . However, the Cs doping produces blockage of the NiMoO_4 pores leading to smaller surface areas when the Cs concentra-

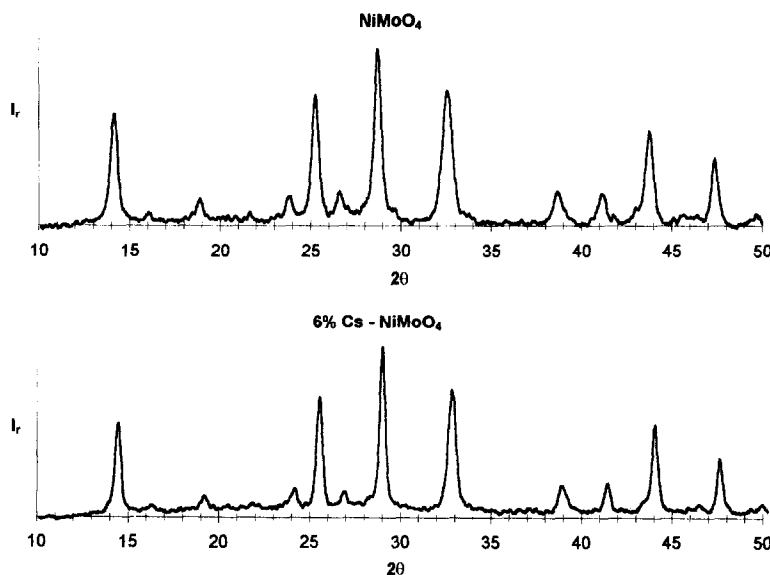


Fig. 1. X-ray diffractograms of α -phases at room temperature for unpromoted and 6% Cs catalysts.

Table 1
XPS binding energies (eV) and atomic ratios for the unpromoted and Cs promoted α -NiMoO₄

Catalyst	Ni		Mo		Mo/	Cs/
	2p _{3/2}	2p _{1/2}	3d _{5/2}	3d _{3/2}	Ni	Mo
NiMoO ₄	856.20	862.77	232.75	235.95	0.97	—
1% Cs-NiMoO ₄	856.25	862.90	232.70	235.87	1.02	0.011
3% Cs-NiMoO ₄	856.33	863.01	232.69	235.80	1.03	0.030
6% Cs-NiMoO ₄	856.40	863.00	232.50	235.70	1.05	0.059

tion increases (Table 2). This surface area decrease is stronger after activation to the β -phase.

In order to clarify the influence of cesium doping on the $\alpha \rightarrow \beta$ transition, an HTXRD investigation was also carried out (Fig. 2). The X-ray spectrum at room temperature is also included in this figure to facilitate comparison.

In the unpromoted NiMoO₄ the transformation from α - to β -phase is apparently complete

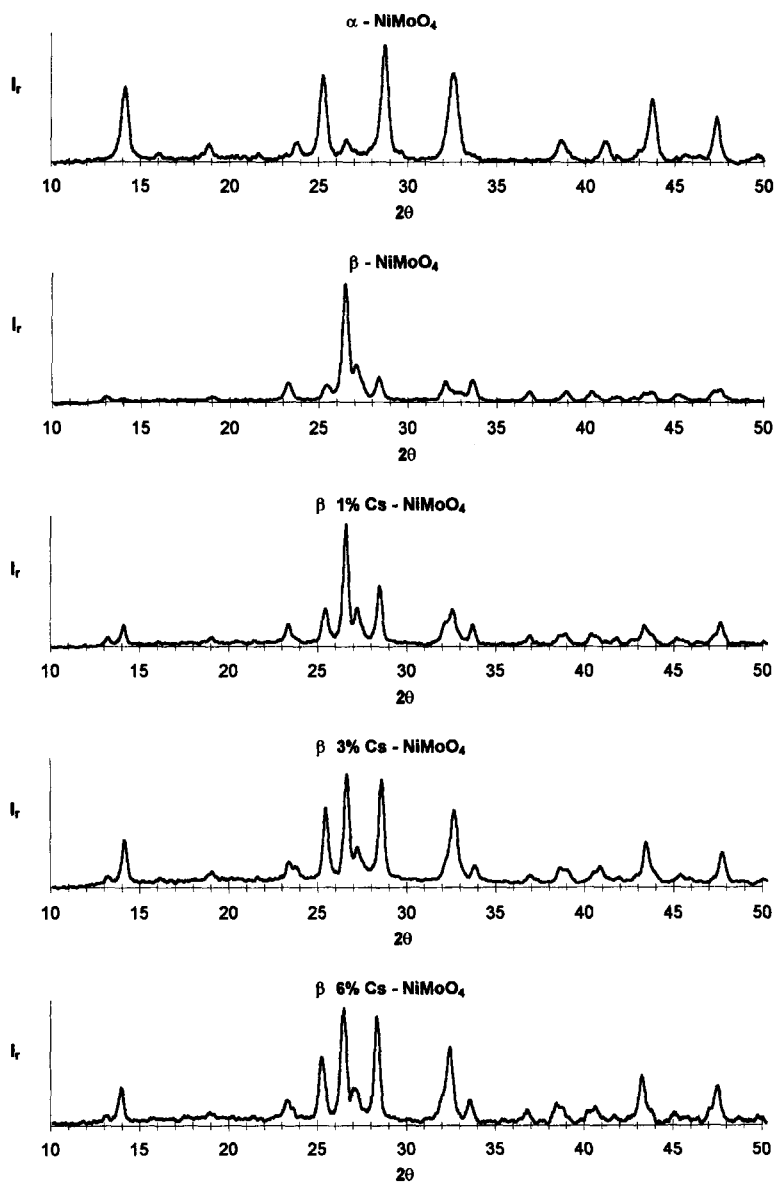


Fig. 2. X-ray diffractograms of α -NiMoO₄ (at 21°C) and all the β -phase catalysts (at 710°C).

Table 2
BET surface areas (m^2/g) of the unpromoted and Cs promoted NiMoO_4

Catalyst	α -Phase	β -Phase ^a
NiMoO_4	44.1	16.0
1% Cs- NiMoO_4	34.9	6.4
3% Cs- NiMoO_4	28.7	4.1
6% Cs- NiMoO_4	26.7	2.5

^a Obtained after $\alpha \rightarrow \beta$ transformation and quenching to ambient temperature.

under the aforesaid conditions, as shown by the relative intensities of peaks characteristic of alpha and beta phases ($2\theta_{I-100} = 28.4^\circ$ and $2\theta_{I-100} = 26.4^\circ$, respectively). Other important α -phase peaks (ASTM – 33-948) are even negligible (14.0° , 43.7° and 47.5°) at 710°C . However, whereas the presence of Cs does not affect the catalyst structure in the α -phase, significant differences are observed in the $\alpha \rightarrow \beta$ transition. In fact the $\alpha \rightarrow \beta$ transition is inhibited by the presence of cesium in the doped catalysts. A mixture of both phases is observed in all the cases, and the α -peaks, weak in the unpromoted catalyst, are again easily identified even with the lower Cs contents. The alpha/beta ratio can be determined by the intensity ratio of the α -phase characteristic peak with respect to the corresponding one of β -phase. It follows the sequence: unpromoted < 1% Cs < 3% Cs \approx 6% Cs. In the case of 3 and 6% Cs doped NiMoO_4 , the phase transition is only ca. 50%.

The catalysts surface was characterized by NH_3 and CO_2 TPD in order to investigate their acid–basic nature. The data obtained are showed in Fig. 3.

In the NH_3 -TPD profile (Fig. 3A), the detector response shows a maximum at about 100°C and decreases quickly at the beginning and more slowly between 200 – 400°C . A second less important maximum appears at around 600°C . These results suggest that besides physical NH_3 adsorption, the catalyst surface also exhibits a certain acidity, possibly involving two main types of sites. However, after this experiment, a change in the sample colour was observed. The

original light green yellow is transformed into blue–purple. This fact suggests the possible formation of nitrogenated compounds which were also observed by Verhaak [15] in other Ni supported catalyst during NH_3 -TPD experiment. Consequently, the acidity estimation by this method could be altered by this reaction and, probably, a less basic adsorbate (e.g. pyridine) must be used.

The CO_2 -TPD experiment for α -phase, with adsorption at 30°C (Fig. 3B) shows that the physisorption of CO_2 is negligible (important detector response was not observed below 100°C) and two types of sites with different

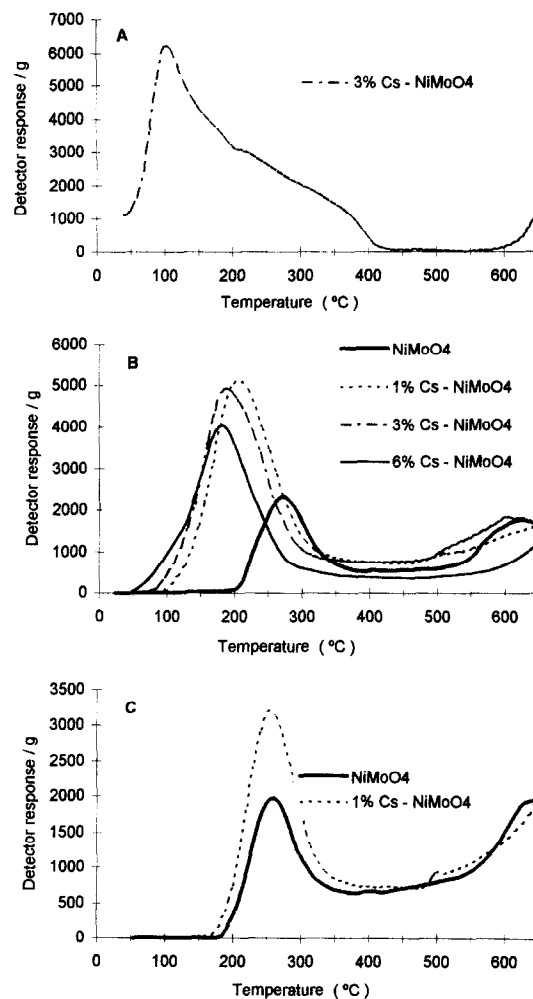


Fig. 3. TPD profile of: NH_3 adsorbed at 30°C (A); CO_2 adsorbed at 30°C (B) and at 250°C (C).

basic strengths are in evidence. The cesium doping causes an increase in the catalyst basicity with respect to the unpromoted NiMoO_4 (visible by the increase in the first peak area) as would be expected according to the electron donor nature of Cs. The peaks tend to appear at higher temperatures with stronger basicity of the surface sites. In our case, the position of the first maximum is progressively displaced to lower temperatures when the alkali contents increases, i.e., the doped catalysts exhibit more

sites than the pure NiMoO_4 , but these new sites are less basic. With respect to the second type, we cannot draw a clear conclusion, partly because the maximum position was never exactly determined since the experiments were performed only up to 650°C to avoid the possible $\alpha \rightarrow \beta$ transition. However, in general, they seem to be displaced to higher temperatures. It is also noteworthy that although the area of the first peak increases with respect to the unpromoted NiMoO_4 for all the doped samples, this

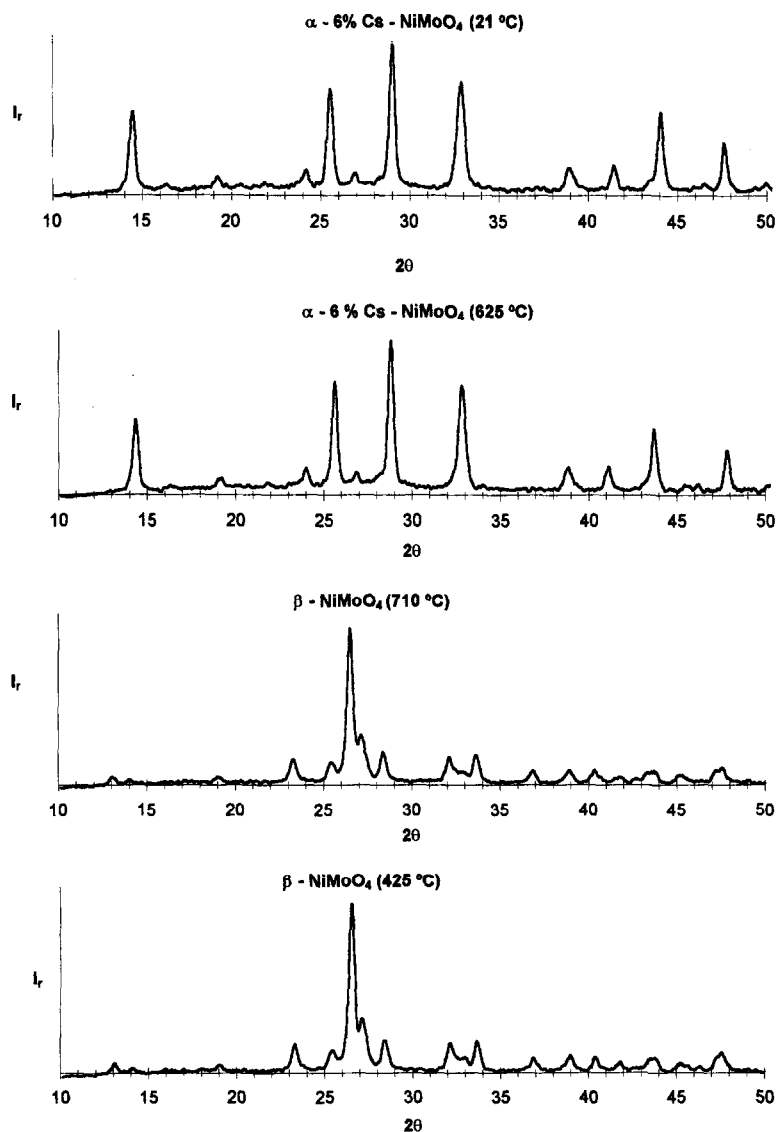


Fig. 4. X-ray diffractograms of α and β phases, showing the stability of the phases.

area is similar for 1 and 3% Cs doped catalysts and significantly decreases in the 6% Cs–NiMoO₄, possibly as a consequence of overdoping.

In order to eliminate the possible effect of physically adsorbed CO₂, the CO₂ adsorption was also carried out at 250°C. The TPD profiles for the unpromoted and 1% Cs doped samples are illustrated in Fig. 3C. A similar increase of basicity is observed although the maxima are logically displaced.

3.2. Catalytic behaviour

The stability of both phases in the temperature range used for catalytic experiments was also confirmed by HTXRD (Fig. 4). It is noteworthy that only dehydrogenation products from butane (C₄'s) and carbon oxides (CO and CO₂) were detected under all experimental conditions. Higher conversions are obtained with α -phase at the same temperature, which agrees with

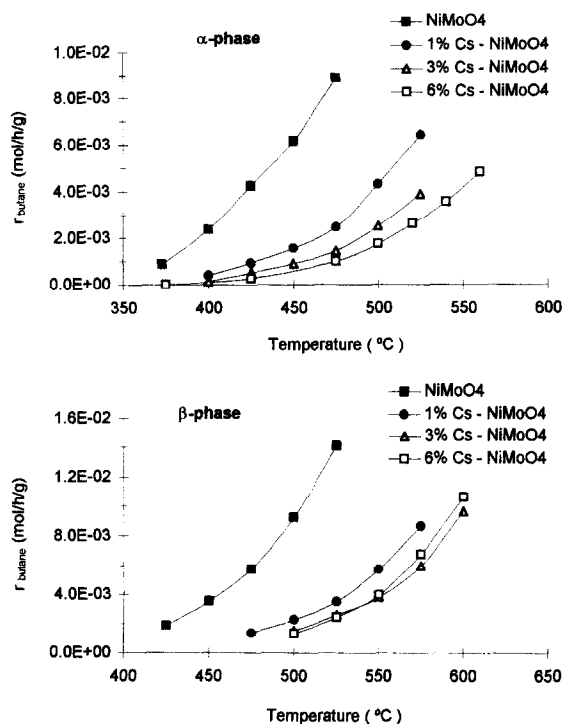


Fig. 5. Dependence of the butane conversion rate on temperature for α - and β -phases.

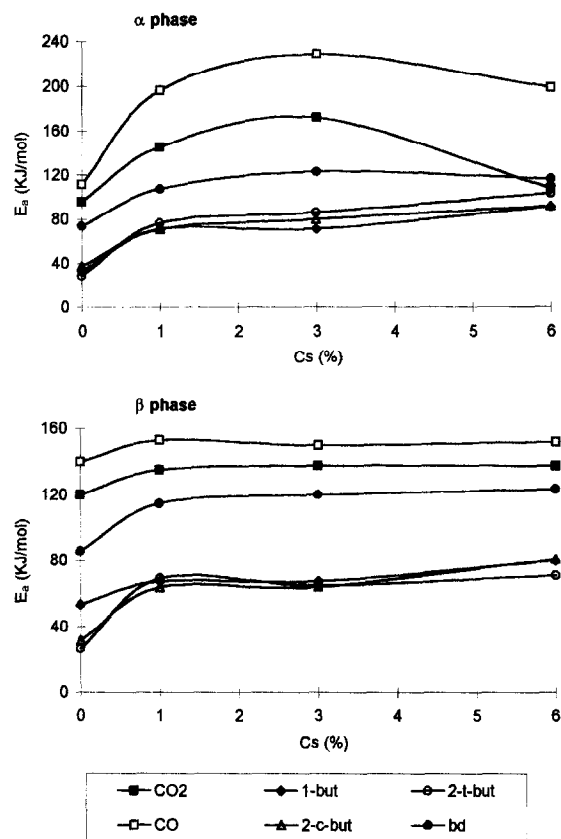


Fig. 6. Dependence of the activation energies on cesium contents for α - and β -phases.

previous studies [1,3]. In general activity decreases for both phases according to the sequence: unpromoted > 1% Cs > 3% Cs > 6% Cs. In Fig. 5 are depicted the rates of butane conversion at different temperatures.

For the experimental conditions used, with conversions low enough to allow computation of reaction rates (r) by the initial rate approach, the representation of $\ln r$ versus $1/T$ for each product shows a linear behaviour with correlation coefficients (R^2) always higher than 0.98. The dependence of the apparent activation energies (E_a) for each product on the cesium contents is presented in Fig. 6. In general, E_a increases for both phases with the Cs doping, leading to activity decrease as mentioned above. It is also important to point out that specially for α -phase, such increase is significantly higher for CO and CO₂ than for C₄'s up to 3% cesium

contents. However, for α -phase, above such dopant concentration, it is observed a decrease in the activation energies for both carbon oxides, being more significant in the case of CO_2 .

In both phases the selectivity increases for 1-butene and 2-butenes up to 3% Cs and after a small decrease is observed for 6% Cs–NiMoO₄. Butadiene selectivity only shows a certain improvement for 1% Cs– α -NiMoO₄, decreasing for both phases with the Cs contents in such a manner that becomes negligible at lower temperatures. The selectivity for both carbon oxides decreases with respect to the unpromoted catalyst at low cesium concentration (up to 3% for α -phase and up to 1% for β -phase) but increasing for CO_2 with the 6% Cs–NiMoO₄ to the level of the unpromoted catalyst (Fig. 7).

When the selectivity to C₄'s is plotted versus the cesium contents at constant conversion (Fig. 7), both phases present an increase for the 1% doped catalyst with respect to the unpromoted NiMoO₄. This effect is more important for α -phase, although the selectivity does not increase

significantly after for the 3% Cs–NiMoO₄. Maxima of selectivity are observed at about 3% Cs for α -phase and 1% Cs for β -phase with well visible decreases at 6% Cs doping.

In Fig. 8 are presented the C₄'s yields vs. the butane conversion for the promoted and unpromoted catalysts. At identical conversions a significant yield improvement is obtained for α -phase with all the promoted catalysts. However, these improvements are less for the 6% Cs–NiMoO₄ catalyst. With β -phase such behaviour is not so evident and only the 1% Cs–NiMoO₄ presents a certain improvement with respect to the unpromoted catalyst.

The catalytic activity of the studied catalysts is clearly in agreement with the structural and chemical features described above.

It was seen that cesium doping inhibits the $\alpha \rightarrow \beta$ transition, decreases the catalyst surface area and increases the catalyst basicity, although overdoping with 6% Cs–NiMoO₄ leads to a decrease in basicity with respect to the other doped catalysts. The effect of this overdoping is

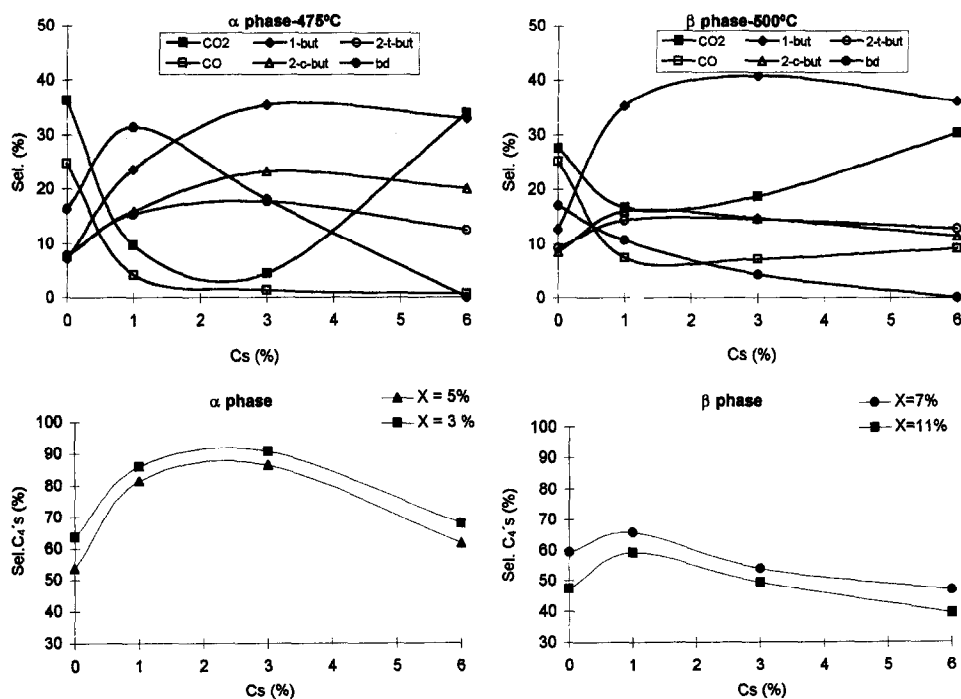


Fig. 7. Effect of surface cesium content on selectivity.

clearly shown by the selectivity evolution. It is well known that the CO_x formation is favoured by an increase in the catalyst acidity [5,16]. In our case, the basicity decrease originated by overdoping induces an increase of carbon oxides formation, mainly CO_2 .

The C_4 's yield increases for α -phase with all the promoted catalysts, but this improvement is less for the 6% Cs– NiMoO_4 due to the overdoping effect. In β -phase, this improvement is only observed with the 1% Cs catalyst, while at greater cesium contents the C_4 's yield even

decreases with respect to the unpromoted catalyst due to the α -phase stabilisation and the overdoping effect.

The effect of surface area decrease is easily eliminated if rates of butane conversion are based on unity surface area (Fig. 9). In such circumstances, the catalytic differences observed when cesium content is changed must originate from different basicities. An increase in the catalyst basicity leads to a decrease in the catalytic activity because the butane–catalyst surface interactions are weakened. So, a signifi-

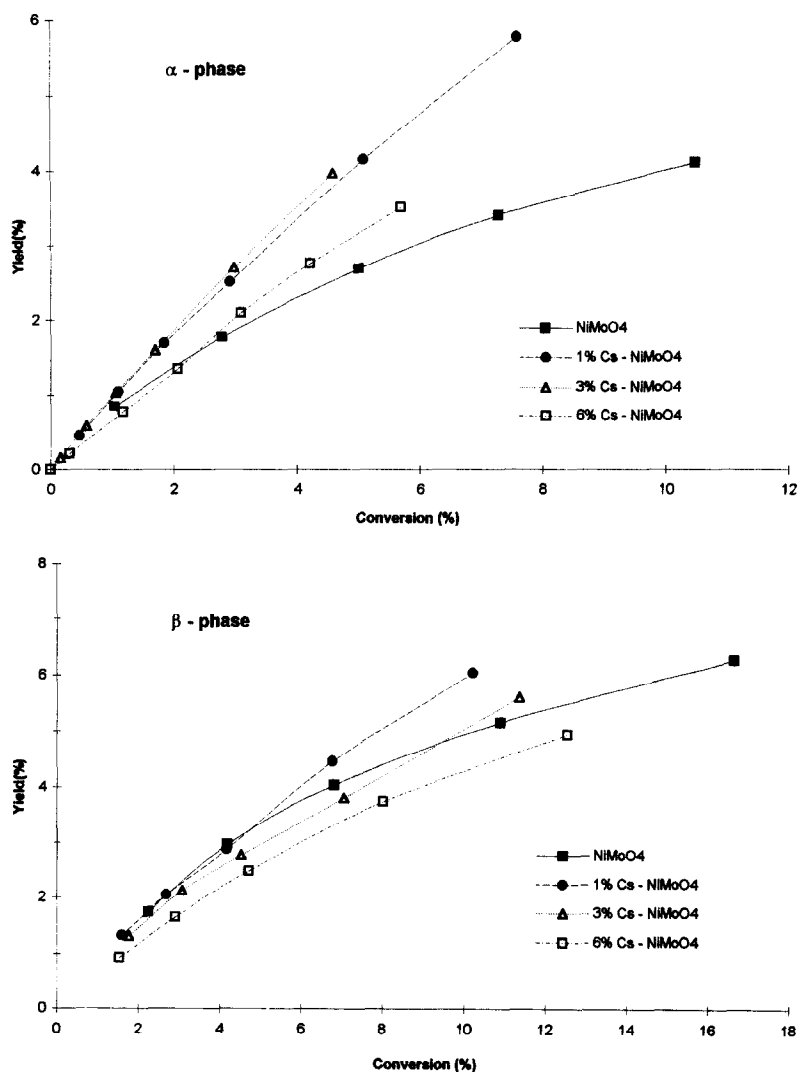


Fig. 8. Dependence of the yield of C_4 's on butane conversion.

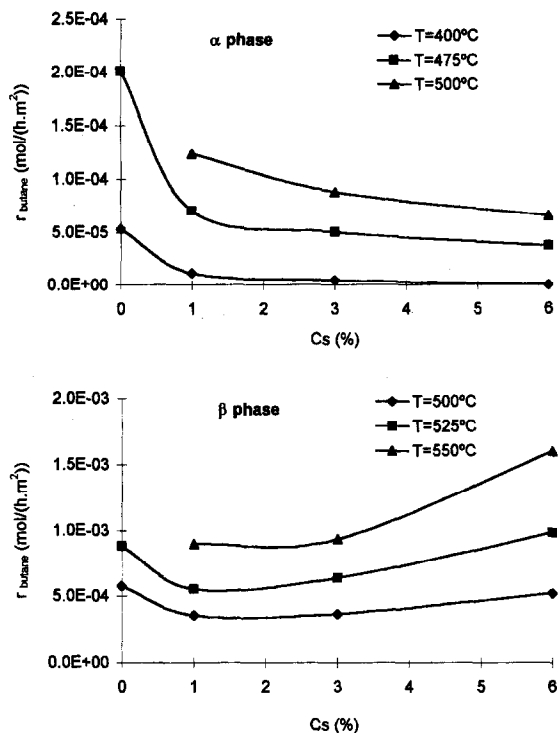


Fig. 9. Influence of cesium surface content on butane conversion rate for α - and β -phases at different temperatures.

cant decrease in the conversion rate is observed at 1% Cs doped α -NiMoO₄ and this decrease attenuates at higher contents of cesium. In β -phase a minimum rate is observed at 1% Cs-NiMoO₄. The increase of the activity normalized to surface area at higher Cs loadings is probably due to overdoping and to the stabilization of the α -phase, as has been noticed by CO₂-TPD and HTXRD experiments, respectively.

4. Conclusions

It has been confirmed by HTXRD measurements that both α - and β -phases of nickel molybdate are stable in the reaction temperature range used for the oxidative dehydrogenation of butane. The doping of NiMoO₄ with cesium does not produce structural changes in the catalyst at room temperature but it restrains the α -to β -phase transition, especially at high concen-

trations of promoter (3 and 6%), for which only 50% transition was achieved. Alkali promoter remains essentially on the catalyst surface, blocking the catalyst pores, thus decreasing the catalyst surface area as the Cs concentration is raised, both for α - and β -phases.

CO₂-TPD measurements with the promoted catalysts evidence that catalyst basicity increases with respect to the unpromoted NiMoO₄. However, a basicity decrease is noticed for the 6% Cs- α -NiMoO₄ due to overdoping.

Such properties of the catalysts are in agreement with the results of the catalytic tests. The catalytic activity decreases for both phases following the sequence: unpromoted > 1% Cs > 3% Cs > 6% Cs. The same trend is observed for α -phase when activity is normalized to surface area. The β -phase shows a minimum at 1% Cs and an increase at higher cesium concentrations. This increase in surface normalized activity possibly emanates from stabilization of α -phase and overdoping. The C₄'s formation is favoured by the cesium presence although in the case of 6% Cs-NiMoO₄ the overdoping leads to an increase of the CO_x selectivity.

Acknowledgements

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