"Pure and modified nickel and cobalt molybdates as catalysts for the oxidative dehydrogenation of propane"

Maione, Andrea

Abstract
This work deals with the search for new molybdate-type catalyst formulations for the activation of light alkanes and their conversion to alkenes. In the first part, we showed that it is possible to stabilize the beta-phase of NiMoO$_4$ (as pure phase) by incorporating a certain amount of Co in its lattice. The sol-gel method was also applied to the synthesis of solid solutions of NiMoO$_4$ and CoMoO$_4$. The main difference between the bulk and silica-dispersed Ni-Co-Mo catalysts prepared by citrate or sol-gel methods as well as impregnation, is related to the fact that it is possible to stabilize the beta-Ni$_{1-x}$Co$_x$MoO$_4$ phase throughout the whole composition range in the dispersed catalysts. Moreover, the catalytic data emphasize the advantage of using mixed Ni-Co molybdates in comparison with simple Ni or Co molybdates and also the fact that a higher activity is reached when these active phases are dispersed in a silica matrix. In the second part, we reported on the synthesis, characterization ...

Document type: Thèse (Dissertation)

Référence bibliographique

Maione, Andrea. Pure and modified nickel and cobalt molybdates as catalysts for the oxidative dehydrogenation of propane. Prom.: Devillers Michel
Chapter I: Introduction
I. General context

Because most intermediates in the petrochemical industry are produced from alkenes and aromatics, the demand of alkenes is increasing, and the existing capacity is becoming insufficient. Until recently, light alkenes have been obtained from steam cracking processes of natural gas and naphtha: these processes are very expensive due to the fact that the obtained products must be separated and purified. Nowadays, research pays attention to the development of new low-cost processes converting light alkanes to valuable products and alkenes by means of oxidation or dehydrogenation processes.

This work deals with the search for new molybdate catalyst formulations, which are known to be active in propane oxidative dehydrogenation, a process which could be replace in the near future the common steam cracking and pure dehydrogenation processes currently used for the production of alkenes.

I.1 Purpose of the work

The main purpose of this work is to investigate and try to rationalize the role played by lanthanides when included in the formulation of Ni and/or Co molybdates catalysts, and the effect that they have on the structure and the catalytic activity in the oxidative dehydrogenation of propane. A second part will be devoted to a study of the influence in the structural properties and the catalytic activity of Ni and/or Co molybdates when dispersed on different supports.

To reach these objectives, the thesis was organized along the following steps:

a) First, a detailed study of the formation of solid solutions of Ni-Co molybdates, as bulk phases by the citrate method or dispersed on silica by sol-gel method (for the main principles of sol-gel method and the application of such a method for the preparation of molybdate-type catalysts see appendix I.2), has been carried out; these phases were characterized in detail from spectroscopic and textural viewpoint and tested for their catalytic activity in propane ODH.
b) Once the Ni-Co-Mo-O-system was understood, we proceeded to the preparation and characterization of some modified simple Ni or Co molybdates, in order to evidence the effect of additional elements like Bi or lanthanides (La, Ce, Pr, Sm, Tb) on the structural and catalytic properties. Comparisons between the bulk modified Ni or Co molybdates obtained by the citrate method and the supported phases prepared by the sol-gel method have been carried out. Finally, some multimodified Ni-Co molybdates containing one or two different lanthanides were also investigated.

c) On the basis of the results obtained in the first part, we performed a study on Ni$_{1-x}$Co$_x$MoO$_4$ dispersed into oxides characterized by different acidities: SiO$_2$, Al$_2$O$_3$, MgO, TiO$_2$, ZrO$_2$ and a mixed Al$_2$O$_3$-MgO support. These catalysts were prepared either by sol-gel or by impregnation with commercial supports.

d) In the final discussion, we will try to rationalize the catalytic behaviour of the complex multicomponent molybdate catalysts by means of correlations with:
- some fundamental physico-chemical characteristics of the promoting elements (ionization energy, absolute hardness and redox potential), that could influence the collective properties of the lattice;
- the textural properties of the solids;
- the acidity of the supports.
For further details on these fundamental physico-chemical parameters see appendixes I.3 and I.4.

It is useful to have a large number of catalysts, guided by knowledge we have gained on the reaction and taking into account ideas present in the literature concerning new preparation methods. These results will be used as our own objectives as described above but could also be used by other investigators in the context of combinatorial chemistry and high throughput experiments.

I.2 Literature Survey
According to the main purpose of the thesis, this introduction is focused on a literature survey concerning:
- the importance of using alkanes as feedstock in industry;
- the advantages and the drawbacks of oxidative dehydrogenation (ODH) vs pure dehydrogenation processes and some paraffins ODH processes that are currently under development;
- the characteristics that a catalyst should have for working properly in selective oxidation reactions;
- the major classes of commonly used catalysts in propane ODH (the reaction selected here) namely: nickel and cobalt molybdate-type catalysts.

**I.2.1 Advantages in using alkanes as feedstock**

An important energy saving is theoretically achieved when comparing the process of direct oxidation of an alkane to a desirable product, to the currently used industrial multi-step process.

A clear example is the synthesis of methanol, which is normally produced through the conventional methane steam reforming process followed by the conversion of syngas to methanol (fig. I.1). If we compare the reaction enthalpies of the direct oxidation of methane to methanol, on one side, and the industrial multi-step process, on the other side, it may appears quite strange to use an endothermic process (steam reforming) to produce first CO and H₂, then followed by an exothermal transformation to the desired product. Another example is the acetic acid process: the first step is the obtention of ethene by steam cracking of natural gas or naphtha, which is then converted to acetaldehyde through the Wacker process, and then oxidized to acetic acid. From the thermodynamical point of view the direct single exothermal transformation would be more appropriate.

Generally speaking, an endothermic process for the production of building blocks always requires very large plants, with high investment costs. New processes can therefore represent a considerable advantage from the environmental point of view with respect to the commonly used multi-step processes. This is the case of the synthesis of methylmethacrylate, which could be produced by oxidation of isobutane to methacrylic acid and the subsequent esterification with methanol. Currently, methylmethacrylate is produced via the acetone-cyanohydrin route, a multistep process with many drawbacks that make it environmentally inadequate. However, it is obvious that thermodynamics cannot rule alone the feasibility of a process, and that the practical conditions allowing the industrial exploitation of new reactions or processes must be fulfilled: achievement
of high productivity and high selectivity, development of stable catalysts, absence of carbon oxides among the by-products, absence of corrosive by-products,...

Fig. I.1: Heat of reaction for some industrial multistep transformations of alkanes to intermediates for the petrochemical industry and for alternative oxidative single-step transformations (1).

Nowadays research is going along the study of new oxidation processes, which could be of industrial interest. Table I.1 lists some alkane oxidation reactions and their stage of development. An interesting process that is expected to be commercialized is the ammoxidation of propane to acrylonitrile (2,3): the key factor is the stability of the product, which preserves it from nonselective consecutive reactions.

The direct production of acrylic acid starting from propane (5-9) is another well-studied process, whose major limitation is due to the very high reactivity of the desired products, which are not stable under the conditions required for alkane activation, and therefore undergo non-selective oxidative transformations.
Table I.1: Some industrial processes and processes under study or development for the oxidative transformation of light alkanes (C₁ – C₄) (4).

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Product</th>
<th>Stage of Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Methanol</td>
<td>Pilot Plant</td>
</tr>
<tr>
<td>Ethane</td>
<td>Acetaldehyde</td>
<td>Research</td>
</tr>
<tr>
<td>Ethane</td>
<td>Acetic acid</td>
<td>Research</td>
</tr>
<tr>
<td>Ethane</td>
<td>Ethylene</td>
<td>Research</td>
</tr>
<tr>
<td>Propane</td>
<td>Acrolein, acrylic acid</td>
<td>Research</td>
</tr>
<tr>
<td>Propane</td>
<td>Propyl alcohol</td>
<td>Research</td>
</tr>
<tr>
<td>Propane</td>
<td>Acrylonitrile</td>
<td>Demonstration Plant</td>
</tr>
<tr>
<td>Propane</td>
<td>Propylene</td>
<td>Research</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Acetic acid</td>
<td>Industrial</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Maleic Anhydride</td>
<td>Industrial</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Butadiene</td>
<td>Industrial, Abandoned</td>
</tr>
<tr>
<td>Isobutane</td>
<td>Methacrylic acid</td>
<td>Pilot Plant</td>
</tr>
<tr>
<td>Isobutane</td>
<td>Isobutene</td>
<td>Research</td>
</tr>
<tr>
<td>Isobutane</td>
<td>Tert-Butyl alcohol</td>
<td>Research</td>
</tr>
</tbody>
</table>

I.2.2 Dehydrogenation versus Oxidative Dehydrogenation

I.2.2.1 Major industrial aspects

As a consequence of their use as starting materials and the decrease in their production because of changes in the operation conditions of the steam-cracking units, research towards the production of alkenes is now proceeding along the dehydrogenation processes of alkanes.

Commercial processes for the synthesis of light olefins through paraffins dehydrogenation are available, essentially for the synthesis of isobutene. In the USA, butadiene is synthesized by catalytic dehydrogenation of n-butane, even if it is usually produced by steam cracking processes. In the case of propane, a couple of plants are on service, while in the case of ethane, thermodynamic constraints would force to operate at impracticable temperature.

These catalytic dehydrogenation processes suffer from several limitations, especially:

- thermodynamic restrictions on conversion and selectivity;
- side reactions such as thermal cracking;
- difficulty in the separation of the alkene from the alkane and other by-products;
- strong endothermic reactions to which large amounts of heat must be supplied;
- formation of coke on the catalysts which need regeneration;
Chapter I: Introduction

- irreversible catalyst deactivation because of the reaction conditions.

In order to overcome these limitations, there are various lines of research:
- optimization of current dehydrogenation technologies, to obtain more selective, stable and environmentally safe catalysts and lower investments and utility costs (10-13);
- dehydrogenation coupled with hydrogen oxidation, to supply the heat of reaction inside the catalytic bed while avoiding overheating, and to shift the equilibrium toward the desired products (14-17);
- oxidative dehydrogenation, to overcome thermodynamic limitations, operate at low temperature and avoid frequent catalyst regeneration;
- use of catalytic membranes to shift the equilibrium allowing high operations at low temperatures (18-21).

The oxidative dehydrogenation process has the potential to overcome the major technical problems associated with pure dehydrogenation, but other problems arise:
- the removal of the heat of the reaction;
- the control of selectivity due to the formation of undesired oxygenated by-products and carbon oxides;
- the flammability of the reaction mixtures;
- the possibility of run-away of the reaction.

From the industrial point of view, the flammability of the reaction mixture in light alkanes ODH is the major constraint in the process, because operating in safe conditions is not optimal for the productivity. It is possible to work in the flammability bell (fig. I.2), present in the diagram for systems like alkane/oxygen/inert, but only by using a fluidized-bed reactor (1), in which the continuous movement of the catalyst inhibits radical chain propagation. Some other important rules must be respected: (i) outside the catalyst bed, the mixture composition must be outside the flammability bell, (ii) the fluidization inside the catalyst bed must be completely homogeneous in order to avoid gas pockets leading to explosions. Because the control of these parameters is very difficult, it is always preferable to operate outside the flammability bell. It is then possible to operate at low alkane-to-oxygen ratio, stoichiometric ratio of alkane to oxygen and high alkane-to-oxygen ratio. In the first case, we are in an uneconomical
situation for the selectivity to the alkene. The second case is preferable because of the high productivity that could be reached even if some drawbacks are present like the difficulties in achieving high conversion of alkane and in controlling catalyst deactivation.

![Flammability Diagram](image.png)

**Fig.1.2:** General flammability diagram for the system alkane/oxygen/inert. The dashed line shows the curve for the stoichiometric oxygen/alkane ratio for the case of alkane dehydrogenation (1).

Most of the papers published in this field report a feed composition close to the stoichiometric ratio; in other cases, large amounts of an inert gas are added to the feed, but this option is quite unrealistic, because the separation of products from the reactants would be very difficult. In the third situation, the hydrocarbon is in excess with respect to the stoichiometric requirement and complete oxygen conversion can be achieved. Moreover, the recycling of unconverted hydrocarbon is usually economical. In this case the main advantage is that the maximum theoretical productivity can be achieved and high paraffin conversion and high alkene selectivity can be reached. The heat released is very high, but the good heat capacity of paraffin (which is always in excess, acting as a ballast) allows a quick exchange of the reaction heat, counterbalancing the exothermic effect.

Another important constraint of ODH from an industrial point of view is due to the reactivity of the intermediate product towards overoxidation under the reaction conditions normally needed to activate the hydrocarbon: oxygenated compounds are precursors for the formation of carbon oxides. If the degree of interaction of the partial
oxidation products and the catalyst surface is weak, then the product may desorb in the
gas phase avoiding overoxidation: consequently the acid-base characteristics of the
catalyst can play a fundamental role in determining the selectivity for the desired
product. Hodnett (22) reported that when the dissociation enthalpy of the weakest bond
in the product is no more than 29.6 - 41.8 kJ/mol weaker than the bond dissociation
enthalpy of the weakest bond in the reactant then the product is obtained with high
selectivity; otherwise the selectivity decreases drastically.

In ODH processes, the choice of the reactor type is critical to control the release
of reaction heat by this exothermic reaction, and to avoid the possibility of runaway
phenomena. Under certain conditions, the heat release is too extensive to be efficiently
removed from the reactor and the increase of temperature leads to a progressive increase
of the phenomenon (CO production is more exothermic than alkene production). The
reactor temperature becomes then hard to control and increases progressively (runaway
up) leading to the rupture or explosion of the reactor.

I.2.2.2 ODH of paraffins to olefins

This section summarizes the most studied ODH processes and the problems
arising during the implementation of these reactions:

a) Oxydehydrogenation of ethane

Among all dehydrogenation processes, the least feasible is the dehydrogenation
of ethane, according to $\text{C}_2\text{H}_6 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$, because it suffers from the most
severe thermodynamic limitations.

In principle, the oxidative dehydrogenation of ethane could constitute a valid
alternative to pure dehydrogenation, but it seems impossible that the ODH process
could replace practically in the near future the steam cracking of naphtha or LPG. The
most important drawbacks are: (i) low selectivity to ethene, (ii) production of CO which
increases the costs for ethene purification, and (iii) the formation of low amounts of
condensable, oxygenated products (acetic acid) which cause corrosion problems and
requires the use of expensive anti-corrosion materials.

b) Oxydehydrogenation of n-butane

Madeira and Portela (23) pointed out the interest of converting n-butane due to
the importance of butanes and butadiene on the international market. Butenes have been
used in gasoline/fuel and in maleic anhydride or butadiene synthesis (24,25). The two possible processes for butane production are the dehydrogenation and the oxidative dehydrogenation. The first reaction is highly endothermic, it requires excess steam to slow coke formation and the effluents contain other products in addition to the desired olefins. Even if n-butane ODH can overcome the well-known thermodynamical limitations, the reaction $\text{C}_4\text{H}_{10} + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_4\text{H}_8 + \text{H}_2\text{O}$ is very complex from the mechanistic point of view. Several consecutive and parallel reactions take place and the formation of oxygenates is very common, so that the maximum yields obtained are still smaller than those obtained in direct dehydrogenation processes.

Because of the complexity of the reactions involved, the research of highly efficient catalyst is not an easy task. Some important aspects like the nature of the active sites, the kinetics and the mechanism of the reaction, the hydrocarbon activation and the factors, which determine selectivity, remain unclear. Moreover, another important key to reach the level of industrial application is the design of an appropriate reactor: the use of a circulating bed reactor, in which the catalyst is reoxidized by oxygen in a regeneration zone after passing through the reaction stage in which the oxidation of the hydrocarbon takes place, is very promising. It is then possible in the future that the combination between a well-designed reactor and a well-projected catalyst will lead to the industrial implementation of n-butane ODH to replace the conventional direct dehydrogenation.

c) Oxydehydrogenation of propane

During the last years, the demand for propene has been increasing: from 1994 to 1999, the demand increased by 5.5% per year. In the U.S.A., the ratio of propene demand to ethane demand grew from 0.48 in 1980 to 0.61 in 2003 (26). About 69% of propene is made as co-product in ethane steam crackers. Propene is the main precursor of a large series of products: polypropylene (39%), acrylonitrile (14%), propylene oxide (11%), cumene (10%), oxo alcohols (8%), isopropanol (7%), oligomers (5%), acrylic acid (3%), others (3%). (See Fig.I.3). Propane ODH takes place in the presence of an hydrogen acceptor such as molecular oxygen in the reaction medium and with the presence of an oxide-type catalyst.
The reactions of interest to compare the direct and oxidative dehydrogenation processes are the following:

a) \( \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2 \) (at 298 K: \( \Delta H^\circ = 111.56 \text{ kJ}, \Delta G^\circ = 86.15 \text{ kJ} \))

b) \( \text{C}_3\text{H}_8 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O} \) (at 298 K: \( \Delta H^\circ = -117.46 \text{ kJ}, \Delta G^\circ = -142.20 \text{ kJ} \))

c) \( \text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O} \) (at 298 K: \( \Delta H^\circ = -2042.01 \text{ kJ}, \Delta G^\circ = -2072.07 \text{ kJ} \))

d) \( \text{C}_3\text{H}_8 + \frac{7}{2}\text{O}_2 \rightarrow 3\text{CO} + 4\text{H}_2\text{O} \) (at 298 K: \( \Delta H^\circ = -1193.93 \text{ kJ}, \Delta G^\circ = -1301.28 \text{ kJ} \))

As indicated, the \( \Delta H^\circ \) and \( \Delta G^\circ \) values of the direct dehydrogenation (a) are positive, whereas those related to the oxidative dehydrogenation (b) are negative: the latter represents a suitable way to overcome the thermodynamic limitation of (a). Equations (c) and (d) represent the main side reactions of an oxidative dehydrogenation process producing carbon dioxide (c) or carbon monoxide (d), and consists of very exothermic reactions.

For propane oxidative dehydrogenation, a “Mars & Van Krevelen” mechanism has been proposed (28-35). This mechanism is composed of five steps, the first one being the rate-determining step:

i) propane adsorption on the catalyst with formation of a bond with a lattice oxygen (O*):
C₃H₈ + O* = C₃H₈O*
ii) propane H abstraction by lattice oxygen:
C₃H₈O* + O* = C₃H₇O* + OH_ads*
iii) formation of propene:
C₃H₇O* = C₃H₆ + OH_ads*
iv) formation of water and a reduced metallic center:
Mox + OH_ads* + OH_ads* = H₂O + O* + M_red
v) oxidation of the reduced metallic center by molecular oxygen:
O₂ + 2M_red = O* + O* + 2Mox

I.3 Hydrocarbon activation

In the past years, many examples of catalysts active in the selective oxidation of paraffins, mainly in propane ODH, were reported in patents and scientific publications. However, low yields in the final product are frequently observed, and the productivity of these processes is therefore far from industrial interest. In order to improve activities and selectivities with the help of an adequately designed catalyst, questions related to the possibility of stopping the oxidation at the desired compound (avoiding overoxidations), and to the importance of the activation mechanism in determining the selectivity of the process have to be addressed (36).

In heterogeneous catalytic oxidation, two different types of heterolytic C-H bond cleavage on the acid-base pair of sites are usually considered (29,37):
1) abstraction of hydrogen in the form of a proton and subsequent formation of a carboanion: \[ \text{C}^\sigma - \text{H}^{+\sigma} \]
\[ \text{M}^{+n} \text{O}^{2-} \]
2) abstraction of hydrogen in the form of a hydride ion and formation of a positively charged hydrocarbon: \[ \text{H}^{+\sigma} \text{C}^{+\sigma} \]
\[ \text{M}^{+n} \text{O}^{2-} \]

In addition, three different mechanisms of homolytic bond rupture are possible:
1) a transition metal ion with electrophilic properties and a vacant coordination site can lead to the formation of a “2e3c” (two-electron three-centers) bond between the C-H bond and the metal;

2) when an easily reducible cation is present at the surface with basic properties, the formation of an alkyl radical and of a proton, with simultaneous reduction of the metal cation can take place.

3) when oxygen radicals are formed on the surface, they can abstract an hydrogen atom generating alkyl radicals.

A disadvantage of ODH is that it requires high temperatures for the activation of the alkane and in the case of propane, the best range of activation temperature is 773-823 K. In order to decrease the high temperatures, a great variety of catalytic systems have been studied. In the present project, the search for new catalysts for this reaction is an interesting challenge, because it is very difficult to limit overoxidation to carbon oxides in the temperature range which is required for the activation of propane.

I.4 Selectivity in hydrocarbon oxidation catalysis

Because selectivity in catalytic oxidation of hydrocarbons is definitively the ultimate goal of the research efforts in that area, there have been many proposals regarding factors that determine selectivity in hydrocarbon oxidation. The following simple scheme may represent the competition between total and partial oxidation of alkanes:

\[
\begin{align*}
\text{O}_2^{\text{gas}} & \rightleftharpoons \text{O}_{2\text{ads}} \rightleftharpoons [\text{O}]_{\text{surf}} \rightleftharpoons [\text{O}]_{\text{lat}} + S \rightleftharpoons \text{SO} \quad \text{(partial oxidation)} \\
& + S \quad + S \\
& \quad \text{(total oxidation)} \quad \text{CO}_2 \quad \text{CO}_2 \quad \text{(total oxidation)}
\end{align*}
\]

In this scheme, O\textsubscript{2\_gas} represents gaseous oxygen, and O\textsubscript{2\_ads} the molecular oxygen species adsorbed on the surface. The latter undergo dissociation with subsequent transformation into active surface species, [O]\textsubscript{surf}, which are in equilibrium with lattice oxygen, [O]\textsubscript{lat}.

The literature shows that the catalysts, which favour total oxidation, are characterized by a high amount of activated oxygen on the surface, while those
favouring partial oxidation are mostly characterized by the intervention of lattice oxygen. A key point is however to clarify the role of the surface active species on the surface ([O]_{surf}).

![Diagram showing oxygen equilibria at the surface of an oxide](image)

**Fig.I.4**: Oxygen equilibria at the surface of an oxide (37).

According to Haber (37), because most transition metal oxides are non-stoichiometric compounds, their compositions depend on the equilibrium between the lattice and the gas phase. A change in oxygen pressure can lead to changes in stoichiometry of the oxide. In presence of point defects, a series of equilibria is established at the surface of the oxide. These equilibria are established between the oxygen atoms present in the bulk and those present in the gas phase (fig.I.4). Among all oxygen species formed on the catalyst surface due to electron transfers between the catalyst and oxygen, superoxide (O$_2^-$), peroxide (O$_2^2-$) and monoatomic ions (O$^-$) exhibiting electrophilic properties, while the lattice oxygen (O$_2^-$) displays a nucleophilic character.

Because the dissociation pressure of the oxide (partial pressure of oxygen) increases with the temperature and there are consequently less adsorbed species at higher temperature, the surface becomes less populated by oxygen atoms, and those that remain on the surface are mainly electrophilic.

When these compounds are used as catalysts for oxidation reactions, they may show high selectivity towards partial oxidation products at low temperatures, because
the surface coverage with electrophilic oxygen species remains low under these conditions. When raising the temperature, the selectivity to partial oxidation products decreases because even if there less adsorbed oxygen species on the surface, they are mainly electrophilic oxygen, favouring total oxidation.

In some strongly depleted oxides like those of molybdenum and tungsten, the change of stoichiometry is accommodated by the formation of shear structures. In this case, there is no vacancy formation when a nucleophilic oxygen is extracted from the oxide surface due to its addition to the hydrocarbon, and either a shear plane is formed, or an existing one grows ensuring the formation of edge-linked octahedral and preserving the normal metal ions coordination. Consequently, only nucleophilic oxygen species remain exposed at the surface. On raising the temperature, the activity increases with an increased mobility of oxygen, but the selectivity to partial oxidation products remains high because of the absence of electrophilic oxygen (38). Quite generally, introducing additional elements into a host oxide lattice may strongly influence its equilibrium oxygen pressure, permitting therefore to modify lattice oxygen mobility and consequently to influence selectivity.

Taking into account all these considerations, Haber (37) divided the catalytic reactions involving oxygen into two groups: electrophilic oxidations and nucleophilic oxidations. The electrophilic oxidations are those in which oxygen is activated into electrophilic species, responsible for the attack of the reactive molecule on its high electronic density sites. The nucleophilic oxidations take place when nucleophilic oxygenated species are added on previously activated molecules.

Besides nucleophilicity and electrophilicity, Kung and coworkers (39) stated that the formation of a certain product can be due to two factors: to the number of the oxygen atoms which are incorporated into the reactant and the place where in the molecule they are incorporated.

A key question is therefore how to control the number of oxygen atoms that are incorporated into the molecule. This number is normally determined by the residence time of the molecule on the surface, by the number of oxygen atoms available at the active sites on that time scale and, of course, by the reactivity of oxygen on the surface (i.e its electrophilicity or nucleophilicity). The number of oxygen atoms available at the active site depends on the diffusivity of the lattice oxygen, and on the size of the surface
species with respect to the size of the site. The reactivity of the oxygen depends on the reducibility of the cation or on the metal-oxygen bond strength.

Moro-oka (40) proposed to use the heat of evaporation of lattice oxygen of the oxide as an estimation of the reactivity of lattice oxygen. If we consider two different active sites, one being a MO$_4$ tetrahedron, and another one consisting of dinuclear M$_2$O$_7$ centers (two corner sharing MO$_4$ tetrahedra), the reactivity of oxygen in these sites can be evaluated by the heat of removal of the lattice oxygen. This heat increases with increasing number of oxygen atoms removed from the site, that is the degree of reduction of the oxide. Actually, two catalysts characterized by these two types of active sites, will show similar selectivities if they show a similar dependence of the reduction heat versus the degree of reduction of the oxide.

1.5 Effect of additives on the physico-chemical and catalytic properties of oxide catalysts in selective oxidation reactions

As one of the main parts of the thesis concerns the effect on the structure and the catalytic activity that some elements like lanthanides can have when introduced in the formulation of nickel and/or cobalt molybdates, this section presents a short literature survey on the importance of adding additives to oxide-type catalysts and how they affect the structural and catalytic properties.

It is well known that industrial catalysts for selective oxidation reactions are normally very complex systems derived in most cases from oxides of vanadium or molybdenum in combination with comparable amounts of other elements. Beside the main components, which constitute the active phase, those catalysts contain a wide range of small amounts of additives. It is recognized that they exert a promoting effect on the activity, selectivity, and lifetime of catalysts, although the detailed mechanism of their action is usually unknown.

As we have already pointed out before, selectivity depends on: i) the forms and properties of oxygen participating in the reaction: chemisorbed, electrophilic species promoting total oxidation and lattice, nucleophilic oxygen mainly promoting selective oxidation; and ii) acid-base properties which, on one hand, may control, desorption of intermediate selective oxidation products and, on the other hand, may determine
adsorption of reactants leading to total combustion. The use of additives can change both properties of the oxygen participating to the reaction and the acid-base properties of the active phase of the catalyst.

**Effect of additives on structural and electronic properties**

Additives are normally introduced by mixing their soluble salts with precursors of active components in a coprecipitation or impregnation step of the catalyst preparation, or are added to the preformed catalyst by impregnation and/or mechanical treatment. Of course the preparation method as well as the calcination treatment can affect the location of additives and consequently the structure and the properties of the catalysts. When incorporated in the bulk of an oxide, these additives, of different valencies from that of host cations, may give rise to point defects. At very low additive concentrations, this modifies mainly the electronic properties of oxides. At higher concentrations, both the structure and the structure-related properties may be changed. The additives can form solid solutions with the main oxide phase, for example in the case of Bi$_3$FeMo$_2$O$_{12}$ when iron is introduced into Bi$_2$(MoO$_4$)$_3$, or in the case of CoTe$^{IV}$MoO$_6$ ad CoTe$^{VI}$Mo$_3$O$_{13}$ (41,42) when Te is introduced into CoMoO$_4$: both the acidic properties and oxygen mobility are modified in the Te-containing molybdates and the resulting new phase behaves better than CoMoO$_4$ in alkene oxidation.

**Modification of activity and selectivity by additives**

The modification of selectivity on introducing additives in oxide catalysts has been mainly discussed in terms of acid-base properties. Additives may affect the acid-base properties by changing the electron density around metal and oxide ions. One can expect that additives of lower electronegativity than that of the active cation in a Me-O couple would shift the electrons towards the active center, rendering it less acidic and more basic. The inverse effect will occur with more electronegative additives. The decrease of the acidity in vanadia-titania catalysts with addition of Na, K, Rb, Cs (43) and Li, K, Rb (44) has been demonstrated by measurements of acidity probe reactions: cumene cracking and isopropanol decomposition.

When the vanadia-titania system was used as catalyst in propane ODH (43), it was observed that, at 10 % conversion, among the systems containing Li, K and Rb the one characterized by higher basicity displayed higher selectivity to propene. It can be argued that propene, acting as a base, is less strongly held on more basic surface and,
desorbes before reacting further to carbon oxides. For ethane ODH, however, the addition of K to VOₓ/Al₂O₃ (45) was found to decreased the selectivity towards ethene. This could be explained by the lower basicity of ethene as compared with the higher alkenes: the ethene-like intermediate will be only weakly adsorbed on acid sites and desorb more easily from the undoped catalyst. The effect of alkali metals on the selectivity depends therefore on the electron donating or accepting power in a series of homologous hydrocarbons.

Additives may also influence the type of oxygen species present on the surface in equilibrium with gaseous oxygen and the reaction conditions in the reoxidation step. Measurements of surface potential at different oxygen pressures have shown that the addition of K to vanadia-titania and molybdena-titania catalysts hinders the formation of electrophilic O` species (46), which could be another reason for the higher selectivity of the catalysts in propane ODH.

I.6 Catalysts in propane oxidative dehydrogenation

A summary of the catalytic performances of the mostly used propane ODH catalysts is given in fig. I.5.

The three major catalysts classes studied in propane ODH are:

1) Vanadium-based catalysts (for major details see the literature survey in appendix I.1.1):
   Bulk oxides Sb-V, or VOₓ supported on ZrO₂, Al₂O₃, MgO.

2) Niobium-based catalysts (for major details see the literature survey in appendix I.1.2):
   NbVOₓ, or Nb-Mo and Nb-Sb systems.

3) Molybdenum-based catalysts:
   AMoO₄ systems (with A = Ni, Co) and solid solutions as Ni₁₋ₓCoxMoO₄.

The section below will focus on nickel and cobalt molybdate-type catalysts, their crystalline structures, the effect of the preparation method on their structures and catalytic activity, and the advantages of having these phases supported; the effect of the structural characteristics in the catalytic activity will also be reported, as well as considerations on the reaction mechanism of propane ODH on mixed nickel and cobalt molybdates.
I.6.1 Molybdenum-based catalysts

I.6.1.1 General context

Molybdenum-based oxides, which are famous catalysts for the selective oxidations of olefins, have so far received less attention than V-based catalysts in the context of ODH, probably because Mo-based oxide catalysts are believed to be ineffective for abstracting hydrogen which has a higher bond energy. Soon and coworkers (47) prepared and tested in propane ODH a large series of metal molybdates AMoO₄ (A = Mg, Ca, Sr, Ba, Zn, Co, Ni, Mn, Cu) and A₂Mo₃O₁₂ (A = Fe, Bi, Ce, La, Sm, Al, Cr), in the temperature range 703 - 773 K. Most of the tested catalysts promoted the oxidative dehydrogenation of propane to form propene and more than 80% of selectivity was achieved at lower conversions. The catalytic activity strongly depends on the kind of metal cations. Among the all tested molybdates, CoMoO₄ was found to be the most active and selective for the propane ODH. NiMoO₄ showed the highest activity in propane oxidation but was non selective. MnMoO₄ revealed a very poor activity. All metal molybdates whose metal oxides have acid-base properties, such as MgO, CaO, SrO, BaO, La₂O₃, Sm₂O₃ and ZnO, show quite high selectivity to

Fig.I.5: Best yields of propene reported in literature for the various catalysts (10).
Chapter I: Introduction

propene but the catalytic activities were much lower than that of CoMoO₄. Al₂Mo₃O₁₂ and Cr₂Mo₃O₁₂ catalysts were highly active but non selective.

On the other hand, Bi₂Mo₃O₁₂, Fe₂Mo₃O₁₂ and Ce₂Mo₃O₁₂ are well known as active catalysts for the selective oxidation of propene to acrolein, Fe and Ce being involved as additional elements with well adapted redox properties (48). CuMoO₄ was also shown to be active for propene oxidation, with the lattice oxide ions being the active species.

As the Ph.D. thesis will concern mainly the study of Ni and Co molybdate-type catalysts, the structural characteristics and catalytic performances of these catalysts used in alkane ODH will be summarized below.

I.6.1.2 Ni and Co molybdates

We have already mentioned that transition metal molybdates are promising catalysts for the oxidative dehydrogenation of propane and also isobutane (47,49-51). Among all transition metal molybdates, cobalt and nickel are reported to be the most attractive catalysts. Madeira and coworkers (52) have recently dedicated an extensive review to the preparation techniques and the use of nickel molybdate catalysts in selective oxidation. Both nickel and cobalt molybdates display a structural polymorphism, which makes the interpretation of their catalytic properties quite difficult (53-56).

I.6.1.2.1 Crystal structure

NiMoO₄ and CoMoO₄ exist in three different structures and two of them, called α and β phases, are stable at atmospheric pressure (57,58). The main difference between the two phases is the coordination of molybdenum, which is octahedral in the α phase and tetrahedral in the β phase. In both cases mutual conversions between these two phases can be observed according to the experimental conditions.

When stoichiometric α-NiMoO₄ is heated under atmospheric conditions at a rate of 20 K min⁻¹ from room temperature, the β-phase is already present at 868 K, but the α phase is still present at 968 K (51). Using time-resolved XRD Rodriguez et al. (59), investigated the kinetics of the α-NiMoO₄ → β-NiMoO₄ transition. In the experiments at variable temperature, the α→β transformation was observed between 823 and 943 K and its rate showed a strong dependence on the heating rate. At 823 K, the rate of the
α→β transformation is very slow, and after 200 min only 27% of the α-phase had changed into the β-phase. When cooling pure β-NiMoO$_4$ samples, the transition to the other isomorph appeared at 413-393 K but the final temperature had a critical effect on the amount of α-NiMoO$_4$ formed.

In the Co-Mo-O system, the transformation α-CoMoO$_4$ → β-CoMoO$_4$ (59) was found to occur at temperatures between 603 and 683 K, which are considerably lower than those found for the α-NiMoO$_4$ → β-NiMoO$_4$ transformation. When heating β-CoMoO$_4$ at high temperatures, an initial decomposition occurred around 1033-1053 K (weak extra lines appeared in the XRD patterns and they can be attributed to cobalt oxide left in the sample after volatilization of MoO$_3$): these temperatures are higher than those observed for the decomposition of β-NiMoO$_4$ (1003-1023 K). Upon cooling the pure β-CoMoO$_4$ to 298 K, there was however no formation of the other isomorph, in contrast with the transformation seen with β-NiMoO$_4$, suggesting therefore that β-NiMoO$_4$ is less stable than β-CoMoO$_4$. The activation energy associated with the change in the coordination of the metal atoms (O$_h$ → T$_d$) for the α-NiMoO$_4$ → β-NiMoO$_4$ transition is quite high (334 kJ mol$^{-1}$).

I.6.1.2.2 The effect of the preparation method on the structure and catalytic performances of bulk catalysts

One central point of the thesis is to underline the differences from the structural and catalytic point of view to which different preparation methods can lead. The section below is a short overview of the most used preparation methods for the synthesis of molybdate-type catalysts. Beside the different crystalline structures obtained by using different methods, the resulting different catalytic behaviours are also underlined.

Lezla and coworkers (60) prepared Ni-Mo-O catalysts (with Mo/Ni >1 or Mo/Ni <1) in different ways, using different methods like: i) precipitation and ii) evaporation to dryness, for the preparation of precursors characterized by various Mo/Ni ratios (> or < 1); iii) sol-gel, with the formation of a polymeric gel made of citric acid; iv) impregnation, for the obtention of NH$_4$Ni$_2$(MoO$_4$)$_2$OH.H$_2$O precursor, which is normally prepared by precipitation of ammonium heptamolybdate and nickel nitrate and
subsequent impregnation of the dried solid with a solution of ammonium heptamolybdate, and v) mechanical mixture by which the precursor \( \text{NH}_4\text{Ni}_2(\text{MoO}_4)_2\text{OH}\cdot\text{H}_2\text{O} \) is mixed with MoO\(_3\).

In the XRD patterns of catalysts characterized by Mo/Ni > 1 and prepared by evaporation to dryness method, the orthorhombic phase MoO\(_3\) is present beside \( \alpha\)-NiMoO\(_4\). When these catalysts are heated to 1073 K in air, MoO\(_3\) begins to sublime and in all cases, the catalysts lose weight. The irreversible reduction on stream of pure \( \alpha\)-NiMoO\(_4\) to MoO\(_2\) and NiO observed for higher contact times is inhibited when MoO\(_3\) is present: the presence of \( \beta\)-NiMoO\(_4\) or NiO beside \( \alpha\)-NiMoO\(_4\) does not seem to produce this effect such as MoO\(_3\).

In the case of catalysts with Mo/Ni > 1, the \( \alpha\) phase of NiMoO\(_4\) tested in propane ODH results to be more active and selective than \( \beta\) NiMoO\(_4\). Several experiments in alkene oxidation have already shown that a molybdenum to metal ratio Mo/M greater than one, or in other words the presence of molybdenum oxide beside metallic molybdates enhances their properties. In those catalysts prepared by precipitation or evaporation, the amount of MoO\(_3\) is higher than that present in the catalysts prepared by sol-gel (a polymeric gel made of citric acid), impregnation or mechanical mixture methods. At the same Mo/Ni ratio, the catalysts prepared by precipitation or evaporation to dryness are characterized by the highest selectivity and higher propene yield and they are also more stable on stream.

In a recent paper, Barsan and coworkers (61) described the influence of the preparation parameters on the composition, active phase and catalytic activity of mixed Ni-Co molybdates: when modifying the pH of precipitation between 6.0 and 8.5, the surface area, the bulk composition and the surface composition of the catalysts were changed significantly. The catalyst showing the highest propene productivity at the lowest space-time was that precipitated at pH 8.5.

I.6.1.2.3 The effect of the support

This paragraph will summarize briefly the effect of the support on the structural and catalytic performances of nickel molybdates: the importance of supporting nickel molybdates will be underlined because the stabilization of the \( \beta\)-phase and, consequently, an improvement of the catalytic behaviour are achieved. The importance
of the support which can strongly affects the acid-base properties of the catalyst and consequently the global catalytic activity in alkane ODH will also be pointed out.

Recently it has been found that is possible to stabilize the $\beta$-phase of NiMoO$_4$ on silica at room temperature by a sol-gel route via silicon alkoxides (62,63). The catalytic behaviour in isobutane ODH of the obtained silica-supported catalyst appeared to be somewhat better (in terms of isobutene productivity and of isobutene and methacrolein selectivities) if compared with those obtained with $\beta$-NiMoO$_4$ stabilized by an excess of nickel (64).

Zavoianu and coworkers (65,66) used wet impregnation and direct precipitation methods in order to prepare TiO$_2$- and SiO$_2$-supported NiMoO$_4$. For all catalysts, the characteristics peaks of both $\alpha$- and $\beta$-NiMoO$_4$ could be observed in the XRD patterns, even at room temperature. The $\beta$-phase appeared in very small concentrations in samples prepared by the impregnation method, but it seemed to be particularly stabilized in samples prepared by the precipitation method.

It has been pointed out that in the case of silica-supported NiMoO$_4$, the support has a strong effect on the acid-base properties of the catalysts, as well as the active phase (67-69). The results obtained by NH$_3$-TPD analysis show that supported catalysts are generally less acid than unsupported NiMoO$_4$, with the acidity increasing with the number of monolayers. Catalysts prepared by impregnation show lower concentration of acid sites than those prepared by precipitation. In this second method, the precursor of nickel molybdate is directly formed on the surface and its interaction with the support may have a strong influence on the structure of the active phase. When these catalysts are tested in isobutane ODH, high surface acidity hinders the formation of isobutene, leading to higher amounts of coke and total oxidation products.

I.6.1.2.4 Catalytic Activity

Effect of structural parameters in the catalytic activity of metal molybdates

Generally speaking, molybdates corresponding to AMoO$_4$ (where A = Ni, Co, Mg, Mn, Zn) exhibit specific surface area ranging from 39 m$^2$g$^{-1}$ for Ni to 14 m$^2$g$^{-1}$ for Mn (70). While the surface area has a large effect on the conversion of propane, the activation of propane is surely influenced by the nature of the metal A. Most probably, the nature of the Mo-O bond is influenced by the nature of the adjacent A metal, it is responsible for the activation of propane. By testing some metal molybdates, NiMoO$_4$ was shown to be the best molybdate in the activation of propane and it was concluded...
that Ni present in Ni-O-Mo-O bond leads to a better activation than Zn in Zn-O-Mo-O bond (fig. I.6).

**Nickel molybdates**

Both α and β phases of NiMoO₄ have been tested in the ODH of propane into propene at different temperatures and the catalytic results are listed in table I.2 (79): it can be seen that the selectivity in propene formation for the β phase is twice that of the α phase for similar propane conversion.

![Graph of Selectivity vs. Propane Conversion](image)

Fig.I.6: Propane oxidation over metal molybdates (AMoO₄) (70).

Del Rosso and coworkers (71) observed that aging of α-NiMoO₄ leads to morphological changes which are responsible of an improved selectivity in propane ODH, if compared to the results obtained with the pure α- and β-NiMoO₄ catalysts.

A series of catalysts represented by the formula Ni₁⁺δMo₁−δ/₃O₄, where −1/5 ≤ δ ≤ 1/3, were also investigated in propane ODH (72,73). The activities of these catalysts were found to be highly sensitive to the catalyst composition and increase with decreasing Ni content; selectivity towards propene is independent of the Ni content when the Ni/Mo ratio is less than unity, and decreases linearly with increasing amounts of Ni when Ni/Mo>1.
Table 1.2: Selectivities in various oxidation products at various temperatures (53).

<table>
<thead>
<tr>
<th>NiMoO₄-phase</th>
<th>Temp.(K)</th>
<th>Conv. (%)</th>
<th>CO</th>
<th>CO₂</th>
<th>C₂H₄</th>
<th>C₃H₆</th>
<th>CH₃CHO</th>
<th>CH₂CH₂CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>773</td>
<td>9.6</td>
<td>23.0</td>
<td>21.4</td>
<td>2.0</td>
<td>49.0</td>
<td>0.6</td>
<td>4.0</td>
</tr>
<tr>
<td>α</td>
<td>803</td>
<td>15.2</td>
<td>27.0</td>
<td>21.0</td>
<td>2.0</td>
<td>46.2</td>
<td>0.5</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>833</td>
<td>24.8</td>
<td>32.2</td>
<td>24.6</td>
<td>2.0</td>
<td>37.5</td>
<td>0.2</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>773</td>
<td>7.2</td>
<td>10.3</td>
<td>8.0</td>
<td>0.7</td>
<td>78.1</td>
<td>0.3</td>
<td>2.5</td>
</tr>
<tr>
<td>β</td>
<td>803</td>
<td>12.5</td>
<td>12.0</td>
<td>10.1</td>
<td>1.0</td>
<td>73.0</td>
<td>0.7</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>833</td>
<td>20.8</td>
<td>18.0</td>
<td>14.0</td>
<td>1.3</td>
<td>63.1</td>
<td>0.3</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Feed: 15% C₃H₈ + 15% O₂ in N₂; Total feed 15 lh⁻¹ for 500 mg of catalyst

Mixed Ni and Co molybdates

Binary metal molybdates containing nickel do not exhibit any activity synergism over the proper reactivity of NiMoO₄ itself. However, it appears to be some synergy between Ni and Co: comparing the results of the simple metal molybdates with those of the binary metal molybdates, indicates that the Ni-Co system is the most active of all the binary systems considered (70). A study of the influence of the A/Mo ratio reveals that the catalytic activity and non-COₓ yield are really sensitive to the Mo content, particularly in the Ni-based molybdates, while the Co-molybdates are less sensitive to this parameter. CoMoO₄ is a well-known catalyst for converting propene to acrolein: high activities and non COₓ yields in the ODH of propane are obtained only at low Mo content. The Mo-rich composition can provide an easy adsorption of propene forming acrolein which is readily converted in COₓ; in addition, the chemisorbed propene can prevent the interaction of propane with the surface, resulting in self-poisoning. It appears that the oxygen between Mo and A metal in the A-O-Mo-O site is the actual abstractor of the rate-limiting methylene hydrogen from the propane.

The Mo-rich compositions are the least active among the molybdates because the concentration of A-O-Mo-O sites on the surface is the lowest. As the Mo concentration increases, the amount of the surface MoO₃ can become significant and ultimately excessive, with the result that the catalyst begins to act as it were simply MoO₃ supported on AMoO₄. The selectivity to non COₓ products is highest for the Mo-rich catalysts. A possible explanation is that the catalysts with low Mo content possess a high surface concentration in metal A, which can lead to the formation of surface A-O-A moieties and higher A-O-A clusters. Therefore, the surface of A-rich compositions retains and oxidizes the formed propylene more readily than the surface of the stoichiometric or Mo rich-compositions.
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Reaction mechanism of propane ODH

Stern and Grasselli (70) investigated the reaction network of propane ODH carried out on a Ni$_{0.5}$Co$_{0.5}$MoO$_4$ catalyst. They observed that the selectivity to partial oxidation products (non-CO$_x$) decreases as the propane concentration increases (100% propene selectivity at 1.5% propane conversion; 76% propene selectivity at 10% propane conversion), but is insensitive to oxygen concentration (74). Propene is the exclusive primary product of propane oxidation, while acrolein, CO and CO$_2$ are formed in a subsequent reaction step, as primary products of propene oxidation. However, while acrylic acid is not a primary product of propene oxidation. The low selectivity to CO and CO$_2$ and high selectivity to acrolein at low propene conversion, coupled with the significantly higher selectivity to CO$_x$ at higher propene conversions, suggests that the majority of CO$_x$ is produced by sequential oxidation of propene through acrolein. Acrylic acid is formed by sequential oxidation of acrolein, and its concentration increases when propylene conversion and acrolein production increases. The vast majority of waste is produced from acrolein overoxidation and minor amounts of CO$_x$ are also formed via the oxidation of propylene. Acrylic acid is produced from the oxidation of acrolein. Propene yield from propane oxidation and acrolein yield from propene oxidation, increase with conversion, reach a maximum value, and then decrease as the hydrocarbon conversion increases. It is assumed as a first approximation that the direct oxidation of propene to CO$_x$ is very limited and only insignificant amounts of acrylic acid are formed, leading to the following simplified scheme of series reactions:

\[
\begin{align*}
\text{CH}_3\text{-CH}_3 & \rightarrow \text{CH}_2\text{-CH}_2 \rightarrow \text{CH}_2\text{-CH-CH}=\text{O} \rightarrow \text{CH}_2\text{-CH-C(OH)}=\text{O}. \\
& \downarrow \text{CO, CO}_2
\end{align*}
\]

Barsan and coworkers (75) studied the kinetic of ODH reaction over mixed Ni and Co molybdates. It was shown that propene selectivity increases when the catalyst works in one of the following conditions: (i) a low oxygen partial pressure, (ii) a high propane partial pressure, (iii) a low propane space-time and (iv) a moderate reaction temperature. They showed that among 11 plausible models, two surface oxido-reduction models are the most adequate for oxidative dehydrogenation reaction. One is a classical Mars-Van Krevelen, in which the rate of the surface re-oxidation step is equal to the rate of the surface reduction step. The first step involves the reaction of propane with one
oxygen species (O) leading to the formation an intermediate, which is then converted to propene. The difference between the two models consists in the surface reduction step in which one oxygen species is involved for one model, while two oxygen species are necessary for the other. Moreover, it was shown that propane and propene compete for the same adsorption sites, propene competing more efficiently than propane and that lattice oxygen is involved also in the formation of carbon oxides (CO and CO₂). By comparing the adsorption with the desorption rate of each compound, it has been clearly demonstrated that: (i) the propane desorption rate is slower than the propane adsorption rate for all propane concentrations, (ii) for 4 % O₂, the oxygen adsorption rate is slower than the oxygen desorption rate, while the reverse situation is true for 6 and 8% O₂ in the feed, (iii) the propene desorption rate is slower than the propene adsorption rate for all propene concentrations, and (iv) the carbon monoxide adsorption rate is slower than the desorption rate for all CO concentrations.

I.6.1.3 Molybdena supported on different oxides

Supported-molybdenum oxide has always been object of research (76-81) with an interesting study on various oxides by Meunier and coworkers (82), in which catalysts consisting of molybdena (5 wt %) supported on different oxides (niobia, alumina, zirconia, silica, magnesia and titania) have been compared for propane ODH.

The zirconia-supported catalysts were much more active than the others but gave high proportions of carbon oxides and lower selectivities to propene at higher conversions. The catalysts based on titania, zirconia and niobia tend to give 100% selectivity to propene at low conversions. No improvement of the propene selectivity of ZrO₂-supported MoO₃ was observed when the molybdenum loading was increased.

Results obtained with different supports loaded with 5 wt.% molybdenum show that titania-supported molybdena was the most selective catalyst at isoconversion. By increasing the molybdenum content on zirconia or alumina, whose specific surfaces are higher than titania, no better selectivity could be found than with titania. Above the monolayer coverage, distorted molybdena crystallites appeared in addition to the previous species and these become more regular in shape with increasing loading. By adding some alkali promotors to those catalysts, an increase of selectivity to propene with increasing basicity of the catalysts was observed: probably a lower surface acidity facilitates propene desorption before further oxidation.
I.7 Lanthanides in catalytic oxidation

Another essential part of this work concerns the study of the effect that lanthanides can have when added to the formulations of nickel and cobalt molybdates. Consequently, this section will be focused on the role that lanthanide oxides, alone, have in catalytic oxidation reactions, and on trying to underline the reasons why they have been chosen as additives to be incorporated in nickel and cobalt molybdates.

When used as pure phases, lanthanide oxides are usually more active in total than in selective oxidation, with a special interest for the non stoichiometric oxides (Pr$_6$O$_{11}$, Tb$_4$O$_7$ and CeO$_2$) (83). A correlation between the catalytic activity and the corresponding oxygen exchange rate was established, in line with the easy conversion Ln$^{3+}$/Ln$^{4+}$.

However, some formulations involving molybdenum (lanthanide molybdates) were shown to play an important role in selective oxidation, like Pr-Mo-O (84) and Bi-Ln-Mo-O (L� = La, Pr, Ce, Sm) phases (85-90). Kremenic and coworkers (84) studied the behaviour of Pr-Mo-O binary phases in the selective oxidation of propene: they observed that the selectivity towards acrolein reached a maximum when 0.8<(Mo/Mo+Pr)<0.88. They discovered that keeping the (Mo/Mo+Pr) equal to 0.88 and adding some bismuth in order to obtain a Bi/Mo ratio equal to 0.075, the selectivity towards acrolein could be improved further: this is due to the formation of the Bi$_2$Mo$_3$O$_{12}$-phase.

Brazdil and Grasselli (89) evaluated the catalytic performances of Bi$_2$-$_x$Ce$_x$(MoO$_4$)$_3$ solid solutions in propene ammoxidation. The catalysts displaying the best catalytic activity are those characterized by $x$ values equal to 0.2 and 1.125. According to these authors, the activity improvement could be due to the enhancement of oxygen and electron transfers because of the presence of the redox couple Ce$^{4+}$/Ce$^{3+}$ close to the active “Bi-Mo” sites.

Han and coworkers (91) investigated the influence of cerium oxides incorporated in the scheelite structure of bismuth molybdate as catalysts for the selective oxidation of propene. In the multicomponent bismuth molybdate catalysts having the scheelite (ABO$_4$) structure, the cation A is usually divalent and eightfold coordinated by oxygen atoms, while the B cation is hexavalent and appears as discrete BO$_4$ tetrahedra in the structure.
The lattice vacancies in the structure are very important in scheelite-type catalysts. The suggested role of the cation vacancy is to stabilize protons formed in the rate-determining dissociative adsorption of propene into a π-allyl intermediate. The initial chemisorption occurs on coordinatively unsaturated molybdenum centers, while allylic hydrogen abstraction takes place on oxygen bonded to bismuth. In addition, cation vacancies generate functionalities, which are responsible for the insertion of oxygen into the allylic intermediate. An increase in the concentration of cation vacancies therefore accelerates the migration of the lattice oxide ions. It would
consequently be possible to control the oxidation activity of such catalysts by controlling the lattice oxygen mobility under catalytic oxidation conditions.

The introduction of the Ce$^{3+}$ on the surface of the scheelite-based oxides can improve the reduction – oxidation process. In the formulation of a good catalyst, the redox functions for controlling the oxidation state of the elements and for activating molecular oxygen are very important. For instance, the promotion effect of cerium (III) oxide on the properties of a complex multicomponent catalyst containing also Bi$_2$Mo$_3$O$_{12}$/ Na$_{0.5-3x}$La$_{0.5+3x}$MoO$_4$ is shown in fig.I.6. (91). The redox couple Ce$^{3+}$/Ce$^{4+}$ assists oxygen and electron transfer in every phase in the supported catalysts.

According to the comments above, lanthanides have been chosen as additives in our molybdate-type catalysts firstly because of the properties of Ln$^{3+}$/Ln$^{4+}$ redox couple, which can actually lead to higher catalytic activity expressed in terms of hydrocarbon conversion, and secondly for the possibility that the formation of ternary phases like Ln-Mo-O could also improve the selectivity towards the desired product.

I.8 Methodology of the thesis

The purpose of this section is to explain the methodology used to reach our objectives and describe the major sections of the thesis. We will justify our choices in carrying out experiments and implementing the characterization techniques.

I.8.1 Solid solutions of Ni and Co molybdates in silica-dispersed and bulk catalysts prepared by sol-gel, impregnation and citrate method: characterization and catalytic activity in propane oxidative dehydrogenation

The role of Ni molybdates and Co molybdate as catalysts in propane ODH is well known. In the case of NiMoO$_4$, the $\beta$-phase, normally quoted as the most active phase, is metastable at room temperature; up to now, this phase was stabilized only by using an excess of nickel (64) or by supporting it on silica and titania by sol-gel, impregnation or coprecipitation method (65-69). The last two methods always give a certain percentage of $\alpha$-phase besides the $\beta$-phase. The obtained catalysts have been tested in isobutane ODH.
We will show that it is possible to stabilize the $\beta$-phase of NiMoO$_4$ by incorporating a certain amount of Co in its lattice.

The chemical literature related to the solid solutions of Ni and Co molybdates is quite scarce. Up to now, only Stern and Grasselli (70) briefly reported on the structural properties and catalytic performances of these solids, underlining that the catalytic activity of NiMoO$_4$- catalysts is equal or even better than that of the solid solutions. We decided to carry out a detailed study of the characteristics of these catalysts when they are prepared as bulk phases by the citrate method and when they are supported on silica by means of sol-gel or impregnation procedures.

Taking into account that:

1) We firstly prepared Ni$_{1-x}$Co$_x$MoO$_4$-catalysts ($x = 0, 0.25, 0.5, 0.55, 0.6, 0.65, 0.75, 1$) by the citrate procedure, which is a classical method for obtaining multimetallic oxides. These compounds have been characterized by XRD, clearly showing the presence of the solid solutions of NiMoO$_4$ and CoMoO$_4$ in a common molybdate lattice as evidenced by the shift of the d-spacing going from NiMoO$_4$ to CoMoO$_4$. Thermodiffractometry experiments have also been performed on pure Ni-molybdate and Co-molybdate in order to check the stability of these phases in the temperature range of interest for the catalytic tests. Because of the lack of spectroscopic data on solid solutions of Ni and Co molybdates, all samples have been analyzed by Raman, UV-vis diffuse reflectance and X-ray photoelectron spectroscopy. The specific surface areas ($S_{BET}$) have been also determined.

2) We then proceeded to the preparation of mixed Ni and Co molybdates dispersed in a silica matrix by a sol-gel procedure, by changing the loading of active phase on silica (Mo/Si molar ratio was equal to 20, 10 and 5). XRD confirmed also here the presence of solid solutions of NiMoO$_4$ and CoMoO$_4$ dispersed in silica. Raman spectroscopy was used to evidence the interaction of the molybdates with silica and XPS was performed in order to evaluate the dispersion and accessibility of the active phase in the catalyst. The specific surface areas, pore size distributions and total pore volumes of all samples were measured.

3) All sol-gel prepared catalysts were tested in propane oxidative dehydrogenation in order to have an idea of the catalytic activity and also to verify if the dispersion of the molybdates on a support could lead to enhanced catalytic performances, in comparison with the catalysts prepared as bulk phases by the citrate method.
4) The last section of this chapter was devoted to the preparation of silica-supported Ni$_{1-x}$Co$_x$MoO$_4$ (Mo/Si = 5) by an impregnation procedure, in order to investigate the influence of the preparation method on the metal dispersion, the textural properties, and the subsequent catalytic performances in propane ODH.

I.8.2 Modified Ni and/or Co molybdates by bismuth and/or lanthanides: characterization and catalytic activity in propane ODH

The literature reports examples indicating that the properties of molybdate-type catalysts can be modulated by the incorporation of additional elements. When stoichiometric nickel molybdate was doped by introducing basic promoters (K$^+$, Ca$^{2+}$), the resulting surface modification led to improved catalytic performances in butane ODH. Kaddouri et al. (92) demonstrated that in the case of propane ODH, the addition of potassium, calcium or phosphorus increased the performance of Ni-Mo-O system in terms of propene selectivity and propane conversion; those promoters not only prevented propane degradation, but also decreased the temperature gradient in the catalyst bed. The latter parameter was also shown to be crucial in the case of isobutane activation, because the high reactivity of the formed isobutene is controlled by the addition of potassium, which avoids its rapid degradation.

The presence of TeO$_2$ and Te$_2$MoO$_7$ next to NiMoO$_4$ was reported to increase the reduction rate of the catalyst and propene oxidation (93), the reduction rate being significantly affected by the nature of the doping element. The results showed that the addition of TeO$_2$ and Te$_2$MoO$_7$ increases the oxygen depletion rate of the system. In the presence of TeO$_2$ and Te$_2$MoO$_7$, Ni-Mo-O systems give rise to enhanced propene conversion and acrolein selectivity with respect to undoped systems. Ni-Te-Mo-O catalysts have been found to have a reducibility trend which fits well with the acrolein and acrylic acid formation from propene oxidation in presence of molecular oxygen.

Considering, on one hand, the great interest of promoting the catalytic activity of Ni and Co molybdates, and taking into account, on the other hand, the catalytic activity displayed by bismuth- or lanthanide-based oxides in partial oxidation reactions, we prepared and characterized Bi and/or Ln- (La, Ce, Pr, Sm, Tb) modified Ni, Co and mixed Ni and Co molybdates, and to investigate their catalytic behaviour.
We have proceeded as follows:

1) Modified Ni(Co)-Ln(Bi)-Mo-Si catalysts (Ln = La, Ce, Pr, Sm and Tb) were prepared by sol-gel method according to the following stoichiometry: 1:1:2.5:20. XRD showed that the identification of the crystalline phases present in the solids were very difficult, due to the low loading on silica and also to the low calcination temperatures. The catalysts were then calcined at two different calcination temperatures and characterized once again by XRD, Raman and X-ray photoelectron spectroscopies. To facilitate the interpretation of these results, catalysts characterized by the same formulations and stoichiometries and some pure reference phases were prepared by citrate or ceramic methods and characterized by XRD, Raman spectroscopy and XPS. After preliminary catalytic tests of the sol-gel catalysts calcined at the lowest temperature, catalytic runs of the complete series of modified catalysts calcined at higher temperature have been carried out.

2) Considering the promising catalytic performances of mixed Ni and Co molybdates, it has been decided to modify these solid solutions by adding lanthanides or bismuth (Ni-Co-Ln-Mo-Si). A complete series of catalysts was prepared by sol-gel method, characterized by means of XRD, Raman spectroscopy and XPS, and tested in propane ODH.

3) Because the catalytic performances of some Ln-modified Ni-Co-Mo-Si samples were clearly improved with respect to the non-modified systems, we decided to involve two different lanthanide elements, or one lanthanide together with bismuth, in the catalyst formulation.

4) After the catalytic tests, some catalysts were characterized once again by XRD and XPS, in order to evidence eventual changes of crystalline phases or surface composition during the catalytic reaction. XPS was also used as a tool to evaluate the amount of carbon formed on the surface of the used catalyst.
I.8.3 Preparation and Catalytic Activity of Ni-Co molybdates supported on alumina, magnesia, titania, zirconia and mixed alumina-magnesia

As a consequence of detailed investigations on nickel and cobalt molybdates obtained ether as bulk or dispersed on silica by sol-gel and impregnation method, we decided to synthesize solid solutions of Ni and Co molybdates dispersed on different supports such as Al₂O₃, MgO, TiO₂, ZrO₂ and Al₂O₃-MgO. Al₂O₃ is a very acidic support and on the other hand MgO is a basic support: it has been previously reported that the degree of acidity of a catalyst plays a fundamental role in ODH reactions, because an acid catalyst better adsorbs the reactant on its surface, leading to a higher catalytic activity but also lower selectivity, as a result of too strong interactions that favour subsequent overoxidation of the products. On the contrary, because basicity favours the desorption of the intermediate products, basic catalysts are usually more selective but less active. Solid solutions of Ni and Co molybdates were finally prepared as dispersed phases in a mixed support Al₂O₃-MgO, in order to optimize the activity and selectivity.

We proceeded as follows:

1) Al₂O₃- and MgO-supported Ni₁₋ₓCoₓMoO₄ were prepared by sol-gel and impregnation methods and the obtained samples were characterized by XRD, Raman spectroscopy, XPS, specific surface area and porosity determination. The catalysts were all tested in propane ODH.

2) To optimize the activity and selectivity of the catalysts, Ni₁₋ₓCoₓMoO₄ samples were prepared by a sol-gel procedure on a mixed Al₂O₃-MgO support, fully characterized by the usual techniques and tested in propane ODH.

3) For comparative purposes, some TiO₂- and ZrO₂-supported Ni and Co molybdates were prepared by impregnation method, characterized and tested.