Chapter IV:
Conclusions and Perspectives

IV.1 Conclusions

The first goal of this work was to carry out a detailed and quite systematic study of the synthesis and physico-chemical properties of Ni, Co and mixed Ni-Co molybdates obtained as bulk (unsupported) or dispersed phases. In the latter case, comparisons were established between catalysts dispersed on different supports.

A second objective of this work was to investigate and try to rationalize the role played by lanthanides when incorporated as additional elements in the formulation of Ni and/or Co molybdate catalysts, and the effect that they have on the structure and the catalytic activity in the oxidative dehydrogenation of propane.

The first part of the conclusions summarizes the results obtained from the structural and textural point of view, underlining the positive effect of the sol-gel method in stabilizing the pure β-phase of $NiMoO_4$ as well as the same beneficial effect obtained by incorporating a lanthanide in the structure of such a molybdate. In the second part, the positive effect, from the catalytic point of view, of preparing solid solutions of Ni and Co molybdates as well as incorporating a lanthanide in the molybdate lattice generally leads to improved catalytic performances.

Structural and textural results

The sol-gel method has been successfully applied to the synthesis of solid solutions of $NiMoO_4$ and $CoMoO_4$. The main difference between the bulk and the silica-dispersed Ni-Co-Mo catalysts prepared by citrate method or obtained by sol-gel or impregnation on commercial supports, is related to the fact that it is possible to stabilize the β-$Ni_{1-x}Co_xMoO_4$ phase throughout the whole composition range in the dispersed catalysts, whereas this was not the case at low Co content in the unsupported catalysts, where a mixture of α and β-phases was observed.

The experiments we carried out, demonstrate that supporting or dispersing the mixed $Ni_{1-x}Co_xMoO_4$ phase on any kind of support (Al_2O_3, MgO, Al_2O_3-MgO, TiO_2 and ZrO_2), leads to the preferential stabilization of the β-phase. The interaction of the molybdenum precursor with the surface hydroxyl group of any kind of inorganic support favors the stabilization of β-phase of $NiMoO_4$ and in the Ni-rich domain of the solid solutions of Ni and Co molybdates.

The stabilization of the β-phase at low temperature throughout the Ni-Co composition range, is very important, because this phase, which is normally metastable at room temperature, is known to display better catalytic performances in alkane ODH.

When the sol-gel method is used for the preparation of the samples, the β-phase is always present. In impregnated catalysts, when simple $NiMoO_4$ is supported on alumina, or titania, the β-phase is partly stabilized but coexists with the α-phase, while the latter appears alone in the ZrO_2-supported catalyst. We can conclude that the sol-gel method can definitely ensure the purity of the β-phase.

Beside the stabilization of the β-phase, dispersing the active phase on different supports, and using different preparation methods, leads to materials characterized by different textural properties. In the case of the silica-based catalysts, the sol-gel method leads to higher specific surface areas, but pore diameter and pore volume are very similar in both sol-gel and impregnated catalysts. Among all the catalysts considered in this work, SiO_2-dispersed catalysts are those characterized by the highest specific surface area and the highest pore volume. In the case of Al_2O_3- and MgO-based catalysts, the sol-gel method results in materials with larger pore diameters. While Al_2O_3-supported catalysts prepared by sol-gel method show a isotherm shape of type II, those prepared by impregnation exhibit a (II+IV)-type shape. There is no such difference between sol-gel and impregnated MgO-based catalysts. Generally speaking, all catalysts prepared by sol-gel method are characterized by higher specific surface areas than the analogous ones prepared by impregnation with commercially available supports.

From a structural point of view, the incorporation of a lanthanide in Ni and/or Co molybdate stabilizes the β-phase for citrate-prepared catalysts except in Sm- and Bi-modified Ni molybdates, in which only the α-phase was detected. Quaternary phases have been postulated in citrate as well as in sol-gel prepared catalysts characterized by the formulation (Ni,Co):Ln(Bi):Mo (1:1:2.5).

In the case of "non stoichiometric" Ni-Co-Ln(Bi)-Mo-Si and Ni-Co-Ln(Bi)-Ln'-Mo-Si catalysts, the situation is unclear. Nevertheless, some hypotheses have been put forward to get an approximate picture of this kind of catalysts. For the first class of catalysts, there are two possibilities: (i) the normal $Ni_{0.5}Co_{0.5}MoO_4$ phase could coexist with the corresponding $Ln_2Mo_3O_{12}$-phases, NiO and CoO; or (ii) the Ln_2O_3-phases could also exist with some MoO_3. For the second class of catalysts, we actually think that the most realistic hypothesis is the one related to the formation of MoO_3 and the two Ln-oxides (Ln_2O_3 or LnO_2, depending on the oxidation state of the additional elements).

Catalytic results

The first part of the thesis was devoted to the comparison of pure and mixed Ni and Co molybdates dispersed on different supports. The propene productivity values of Al_2O_3-based catalysts are very similar in both sol-gel or impregnated catalysts, but the intrinsic propene activity is higher in the sol-gel materials. On the other hand, magnesia-supported molybdates prepared by impregnation display a higher intrinsic propene activity than the analogous ones prepared by sol-gel method, but the propene productivities are very close in both cases. Mixed Al_2O_3-MgO-dispersed catalysts are characterized by performances, which are lower than those of Al_2O_3-supported catalysts and higher than those of MgO-based ones. In the case of SiO_2-supported catalysts, the intrinsic propene activity values are very similar in both sol-gel or impregnated catalysts, but the propene productivity is higher in the sol-gel materials.

The catalytic behaviour of most catalysts could be explained by taking into account the differences in textural properties and surface composition resulting from the different preparation methods: catalysts displaying the higher catalytic activity are those with the largest pore diameter. In the solid solutions of $NiMoO_4$ and $CoMoO_4$, it has also been suggested out that the (Ni/Co) experimental atomic ratio, measured by XPS, could play an important role: the higher the (Ni/Co) experimental ratio, the higher the intrinsic propene yield; however, above a certain limit, high experimental Mo/Support ratios could reveal the formation of surface MoO_3 which could be responsible for lower catalytic activity. It can be definitely concluded that the preparation method acts on the textural properties of the catalysts leading to different catalytic behaviours.

When expressed in terms of propene yield ($YC_3^=$), the order of the catalytic activity according to the support is: $SiO_2 > Al_2O_3 > Al_2O_3$-MgO > MgO for the sol-gel catalysts, and $Al_2O_3 > ZrO_2 \approx MgO > SiO_2 > TiO_2$ for the catalysts prepared by impregnation.

When expressed in terms of intrinsic propene activity ($\mu mol\ h^{-1}\ m^{-2}$), the sequence become: $Al_2O_3 > Al_2O_3$-MgO > MgO > SiO_2 for the sol-gel catalysts and ZrO_2 > MgO > $TiO_2 > Al_2O_3 > SiO_2$ for the catalysts prepared by impregnation. Finally in terms of propene productivity ($mmol\ h^{-1}\ g_{ph}^{-1}$) the sequence is: $Al_2O_3 \approx SiO_2 > Al_2O_3$-MgO>MgO for sol-gel catalysts, and $ZrO_2 > Al_2O_3 \approx MgO \approx SiO_2 > TiO_2$ for the catalysts prepared by impregnation.

The most performing catalysts are those supported on zirconia prepared by impregnation method and this confirms that a medium degree of basicity of the catalyst is a key parameter that controls the adsorption/desorption step of the intermediates in ODH reactions and therefore exerts a strong influence on the performances.

In the second part it has been demonstrated that adding one or two lanthanides to mixed Ni-Co molybdates led to an improvement of the overall catalytic behaviour, in terms of activity and selectivity to propene. The correlations described between the yield in CO_2 or the selectivity to propene and fundamental properties of the additional elements, like ionization energy, absolute hardness and redox potential, confirm that these parameters are useful theoretical tools to account for the global properties of multicomponent oxidation catalysts involving several active elements. When considering the ionization energy, the incorporation of $Ln^{3+/4+}$ in the molybdate lattice affects the polarization of M^{n+}-O^{2-} and consequently the electron density on the lattice O^{2-} anions. In the presence of additional elements with low IE, the average nucleophilicity of lattice oxygen will increase and lower CO_2 yields result. On the basis of the absolute hardness, the results underline the importance of strong interactions between the alkane and the metal cation in order to activate the substrate and convert it into total oxidation products. Based on these considerations, it was observed that the selectivity increase to partial oxidation products could be the consequence of weaker interactions between the catalyst and the formed propene which would desorb more easily from the surface. If the redox potential is considered, the most selective catalysts are characterized by the lowest redox potential: the low reducibility of the M^{n+} cation diminishes the availability of lattice oxygen (O^{2-}) as electrophilic species (O^{-}), promoting thereby partial oxidation.

However, it must be remarked that all Tb-based catalysts promote total oxidation rather than partial oxidation. This is consistent with the fact that reactive oxygen ions would be mainly located in the vicinity of Tb; the global activity of the catalyst would therefore be mainly influenced by the presence of Tb rather than that of the other lanthanide.

Generally speaking, our approach shows the interest of playing with lanthanides in such formulations, because this allows to tune the local electronic properties in an almost continuous way, while taking advantage of the great similarity of their chemical behaviour, which favors the substitutional incorporation in the oxide lattice.

IV.2 Perspectives

Industrial perspectives

In chemical industry, the activity of the catalyst usually decreases with time, a process often related to the loss of active surface areas, which can be caused, among other things, by the adsorption of impurities, by the production of coke in the case of hydrocarbon reactions or by restructuration of the active surface.

According to the XPS analyses after use (see section IV.5 in annex IV), the catalysts prepared in this work, showed no coke formation; nevertheless catalytic tests of long duration should be carried out in order to verify whether the coke formation starts only after many hours on stream.

Long duration tests would also allow us to check whether the catalysts undergo sintering phenomena, a usual drawback of catalysts characterized by high specific surface areas. The great majority of the catalysts prepared in this work are characterized by very high specific surface areas which could, in principle, be the cause of the easy sintering phenomena: surely, the nature of the support could play a role on the ease of such sintering phenomena. In our case, the catalysts characterized by the lowest specific surface area are the TiO_2- and ZrO_2-based ones. The ZrO_2-supported catalysts are the most active ones if we talk in terms of intrinsic propene activity and propene productivity and at the same time they are characterized by an average specific surface area equal to 9 $m^2\ g^{-1}$: they are supposed to be also the more stable in the presence of stream. New and deeper investigations on this class of catalysts, for a future use in industry, should be carried out, taking also into account that there is only little influence of Ni/Co ratio in their catalytic performances.

The problem of propene stability towards consecutive unselective oxidative attacks makes the finding of a suitable catalyst for propane ODH a difficult task. Several systems have been found that can activate the paraffin, but most of them are unable to save the olefin formed. It is well known that molybdates exhibit low activity in propane ODH, but very high selectivity towards oxygenated products. It was observed that the higher the reaction temperature, the higher the catalytic activity and consequently the lower the propene selectivity. In our work, it has been found that modifying mixed Ni-Co molybdates by lanthanides generally lead to improved catalytic performances expressed in terms of propene yield. Nevertheless in such catalysts there is a chance that formed CO_2 could react with the catalyst and lead to the formation of

Ln-carbonates or oxo-carbonates, which could deactivate the catalyst. Long duration tests could also clarify this aspect because the formation of Ln-(oxo)-carbonates can take time.

Another aspect that must be clarified, before considering the possibility to develop our catalysts from an industrial point of view, is the stability over long time of the active phase. It is well known that a multicomponent oxide may decompose into other compounds, sometimes due to the loss of a particular element giving a volatile compound. In the present case, MoO_3 could progressively form during the reaction and evaporate from the catalyst because of the temperature reached in propane ODH.

Table IV.1: Catalytic performances of bulk and supported Ni, Co and Ni-Co molybdate catalysts in propane ODH: comparison with literature data.

Composition and molar ratio	Preparation method	Temperature (K)	Intrinsic propene activity ($\mu mol\ h^{-1}m^{-2}$)	Propene productivity ($mmol\ h^{-1}g_{ph}^{-1}$)
Ni:Mo:Zr 1:1:5	Impregnation	753	143	6.58
Ni:Co:Mo:Zr 0.75:0.25:1:5	Impregnation	753	135	4.65
Ni :Co :Mo :Zr 0.5:0.5:1:5	Impregnation	753	170	5.22
Ni :Co :Mo :Zr 0.25:0.75:1:5	Impregnation	753	132	4.54
Co:Mo:Zr 1:1:5	Impregnation	753	126	3.85
Mg:Mo:Si 1:1:0.77	Impregnation (70)	833	41.4	0.87
Mn :Mo:Si 1:1:0.90	Impregnation (70)	833	62.6	0.88
Zn:Mo:Si 1:1:0.93	Impregnation (70)	833	21.5	0.28
Ni:Mo:Si 1:1:1.1	Impregnation (70)	833	124	4.45
Ni:Co:Mo:Si 0.75:0.25:1:1.1	Impregnation (70)	833	120	3.95
Ni :Co :Mo :Si 0.5:0.5:1:1.1	Impregnation (70)	833	72.3	2.38
Ni :Co :Mo :Si 0.25:0.75:1:1.1	Impregnation (70)	833	29.6	0.71
Co :Mo :Si 1:1:1.1	Impregnation (70)	833	36.1	0.79
(α) Ni:Mo 1 :1	Coprecipitation (93)	833	428	17.1
(β) Ni:Mo 1 :1	Coprecipitation (93)	833	605	24.2
$0.5MoO_3$-P_2O_5/ α $NiMoO_4$	Coprecipitation (93)	806	581	24.4
Ni:Co:Mo 0.5:0.5:1	Coprecipitation (pH = 6.0) (61)	723	58.8	1.35
Ni:Co:Mo 0.5:0.5:1	Coprecipitation (pH = 7.5) (61)	723	11.3	0.68
Ni:Co:Mo 0.5:0.5:1	Coprecipitation (pH = 8.5) (61)	723	22.5	2.31

Table IV.1 compares the catalytic performances of zirconia-supported catalysts, prepared in this work, with those of some molybdate-type catalysts reported in the literature. First of all, the choice of $NiMoO_4$ or $CoMoO_4$ as suitable catalysts for propane ODH seems to be very appropriate: in fact all Ni and Co molybdates display a better catalytic activity than that of $MgMoO_4$, $MnMoO_4$ and $ZnMoO_4$.

Moreover, zirconia-supported molybdates show intrinsic propene yields and propene productivities higher than those of silica-supported molybdates studied by Stern and Grasselli (70) obtained at higher reaction temperature and much higher active phase loading. The choice of zirconia as support for the molybdates seems therefore to be particularly adequate and suggests that the medium degree of basicity of such a support could improve the global catalytic behaviour of the catalyst.

Considering the bulk nickel molybdates, studied long ago by Kaddouri and coworkers (93), the results concerning their catalytic activity show the highest values of intrinsic propene yield and propene productivity ever obtained. When bulk mixed Ni and Co molybdates are prepared at different pH values, they show different catalytic behaviours as demonstrated by Barsan et al. (61); nevertheless their catalytic performances are very far from those achieved by our zirconia-dispersed mixed Ni and Co molybdates.

However, further investigations should be carried out in order to confirm and improve the results obtained in this work, from both the analytical and catalytic point of view. We suggest the following points:

Al_2O_3- and MgO-dispersed Ni and Co molybdates

In the case of silica-dispersed molybdates prepared by the sol-gel method, we have shown that diluting the active phase into the silica matrix (catalysts characterized by a Si/Mo equal to 20) leads to higher propene productivity values. The same investigation could be carried out in the case of Al_2O_3- and MgO-dispersed catalysts by preparing the same samples but varying the (Al,Mg/Mo) ratios. However, it must be taken into account that working with lower amounts of active phases will lead to a progressive loss of structural information (namely by XRD).

TiO_2- and ZrO_2-dispersed Ni and Co molybdates

Ni and Co molybdates have been dispersed on titania and zirconia by means of impregnation method, displaying the highest intrinsic propene yields among all impregnated catalysts. It would be interesting to prepare these dispersed molybdates by sol-gel method, in order to emphasize the eventual differences in the textural properties of the obtained solids and in their catalytic behaviour in propane ODH. Moreover, preparing the same samples but varying the (Ti,Zr/Mo) ratio could allow us to investigate the effect of different degree of dilution of the active phase on the support.

Ni and Co molybdates modified by lanthanides

We have demonstrated that playing with lanthanides in Ni-Co-Ln-Mo-Si systems allows tuning the local electronic properties in an almost continuous way, leading to improved catalytic performances, which could be correlated to some fundamental physico-chemical parameters. However, the formulation chosen for our catalysts were not stoichiometric, since there is a deficiency in Mo. Comparative experiments with Mo in stoichiometric amounts should be carried out.

Use of additional technique: TOF SIMS

A technique which could be used in order to better define the postulated quaternary Ni(Co)-Ln-Mo-O phase is the TOF SIMS (time-of-flight secondary ions mass spectrometry). This technique could perhaps allow us to discriminate fragments characteristic of ternary (Ln-Mo-O or Ni(Co)-Mo-O) and quaternary phases.