Summary

This work deals with the search for new molybdate-type catalyst formulations for the activation of light alkanes and their conversion to alkenes. A first part will be devoted to the study of the influence in the structural properties and the catalytic activity of Ni and/or Co molybdates when dispersed on different supports or modified by different elements. In a second part, attempts to rationalize the influence of additional elements in the catalyst on their performances by referring to fundamental physico-chemical properties is also presented.

In the first part, we showed that is possible to stabilize the β-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 β-$Ni_{1-x}Co_xMoO_4$ 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, with quite appreciable propene productivities at 753 K. When comparing catalysts with the same overall composition but prepared by sol-gel or impregnation methods, it comes out that has their catalytic behaviour does not follow a specific trend: samples prepared by sol-gel method are sometimes more efficient than those prepared by impregnation, and sometimes not.

Then we reported on the synthesis, characterization and catalytic activity of solid solutions of Ni and Co molybdates dispersed on different supports such as Al_2O_3, MgO, TiO_2, ZrO_2 and Al_2O_3-MgO. These experiments demonstrate that supporting or dispersing the mixed $Ni_{1-x}Co_xMoO_4$ phase on any kind of support leads to the preferential stabilization of the β-phase. It was also shown that catalysts characterized by intermediate acid-base properties give better catalytic performances than those with high acidity or high basicity.

Considering the great interest of promoting the catalytic activity of Ni and Co molybdates, and taking into account the catalytic activity displayed by bismuth- or lanthanide-based oxides in partial oxidation reactions, Bi and/or Ln- (La, Ce, Pr, Sm, Tb) modified Ni, Co and mixed Ni-Co molybdates were prepared, characterized and investigated from the point of view of their catalytic behaviour. The incorporation of a lanthanide in Ni and/or Co molybdate stabilizes the β-phase for citrate-prepared catalysts except in the case Sm- and Bi-modified Ni molybdates in which only the α-phase was detected. Concerning the catalytic activity of these solids, it was observed that when solid solutions of β-$NiMoO_4$ and β-$CoMoO_4$ are modified by a lanthanide, a strong enhancement of the catalytic activity and the selectivity towards propene is observed except in the case of Sm. The Tb-modified catalysts display the highest propene productivity, but the most selective catalysts are those modified by La or Pr. Incorporation of Ce strongly improves the catalytic activity, more than propene selectivity. The presence of Bi in the formulation of the catalyst results in a lower propene selectivity.

The catalytic activity of the mixed Ni-Co molybdates modified by one or two lanthanides were finally interpreted by referring to the ionization energy as well as their absolute hardness and redox potential of the additional element. 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. It was found that 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. If the redox potential is considered, the most selective catalysts are characterized by the lowest redox potential.

The correlations described between the yield in CO_2 or the selectivity to propene and fundamental properties of the additional elements, confirm that these parameters are useful theoretical tools to account for the global properties of multicomponent oxidation catalysts involving several active elements.