"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 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
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This chapter provides the necessary information concerning the catalyst preparation, the different characterization techniques, the installation used for the evaluation of the catalytic performances of the catalysts, the reaction conditions and the expressions of the catalytic results. A list of all starting reagents and their purity degree is given in Appendix II.1.

II.1 Catalysts prepared by the Citrate Method (94)

II.1.1 General principles

The citrate method associates randomly all elements in the liquid form, and then minimizes segregation because of the viscosity of the precursor and decomposition in the solid state when diffusion is difficult.

The basic principle of this method consists in combining in aqueous solution, citric acid, an organic acid characterized by strong complexing ability and high solubility in water, with metal ions incorporated in the form of their respective nitrates. After evaporation, a “citrate gel” is formed in which the metal ions are intimately mixed at the molecular level, in an ill-defined polymeric network with bridging citrate ligands. Once dried under vacuum, these complexes constitute precursors of atomically homogeneous multimetallic oxides, obtained after calcination in air. There are two possible mechanisms of decomposition of citric acid: in the first one, oxygen is the oxidant and in the second one, the nitrate ion plays this role:

1) \[ C_6H_8O_7 + \frac{9}{2} O_2 \rightarrow 6 \text{ CO}_2 + 4 \text{ H}_2\text{O} \]
2) \[ C_6H_8O_7 + 6 \text{ NO}_3^- \rightarrow 6 \text{ CO}_2 + \text{ H}_2\text{O} + 6 \text{ OH}^- + 6 \text{ NO} \]

It has been shown that the decomposition mechanism of citrates is preceded by the breaking of M-L (L = ligand) bond, M-OH bond and M-H\text{H}_2\text{O} bond, which are weaker than the one related to M-COO\text{O}^-, responsible for the activation energy of this process.

II.1.2 Preparation of Ni-Co molybdates

Adequate amounts of M(NO\text{O}_3)_2 \cdot 6\text{H}_2\text{O} (M = \text{Ni and/or Co}) and (NH\text{H})_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O} are dissolved separately in water to obtain the molybdate composition Ni_{1-x}Co_xMoO_4 with x = 0, 0.25, 0.35, 0.40, 0.45, 0.50, 0.75 and 1.0, and
(Ni+Co)/Mo = 1.0. An excess of citric acid (1.5 mol citric acid/mol M, M = Ni, Co, Mo) is then added to each solution. The obtained solutions are mixed together and the final solution is concentrated in a rotatory evaporator until formation of a viscous gel, which is then heated at 353 K for 20 h in a vacuum oven. Once a powder has been obtained, the catalyst precursor is pre-calcined at 573 K in a flow of 1 l min\(^{-1}\) of dry air, in order to allow the decomposition of the citrate ion involving the formation of CO\(_2\) and water. After the pre-calcination treatment, the catalyst precursor must be calcined at a temperature determined by thermogravimetric analysis. In our case, the standard calcination conditions are 923 K for 20 h in a flow of 1 l min\(^{-1}\) of dry air.

II.1.3 Preparation of M-Ln(Bi)-Mo catalysts (M = Ni, Co; Ln = La, Ce, Pr, Sm, Tb)

Starting reagents are the metal nitrates: M(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O (M = Ni, Co), Ln(NO\(_3\))\(_3\)\(\cdot\)6H\(_2\)O (Ln = La, Ce, Pr, Sm, Tb), Bi(NO\(_3\))\(_3\)\(\cdot\)5H\(_2\)O and ammonium heptamolybdate, (NH\(_4\))\(_6\)Mo\(_7\)O\(_{24}\)\(\cdot\)4H\(_2\)O. These compounds are dissolved separately in water in adequate amounts corresponding to the following molar composition M-Ln(Bi)-Mo (1:1:2.5). This stoichiometry was chosen because it formally corresponds, after calcination, to an equimolar mixture of MMoO\(_4\) and Ln\(_2\)Mo\(_3\)O\(_{12}\) phases. After adding an excess of citric acid (1.5 mol citric acid (mol metal \(^{-1}\)) to each solution, they are mixed together and the final solution is concentrated until formation of a liquid gel. The obtained gel is then heated at 353 K for 20 hours in a vacuum stove. Once a powder has been obtained, the catalyst precursor is pre-calcined at 573 K in a flow of 1 l min\(^{-1}\) of dry air, then after the pre-calcination treatment, the catalyst precursor is calcined at a higher temperature previously determined by thermogravimetric analysis. In our case, the standard final calcination conditions are T = 923 K for 20 hours in a flow of 1 l min\(^{-1}\) of dry air. Because the TGA of the M-Bi-Mo citrate gels (M = Ni, Co) were found to exhibit an abrupt degradation in the temperature range 673-723 K, the final calcination temperature of these samples was fixed at 823 K.

II.1.4 Preparation of \(\alpha\)-Bi\(_2\)Mo\(_3\)O\(_{12}\) (95) and Pr\(_2\)Mo\(_3\)O\(_{12}\) (96)

\(\alpha\)-Bismuth molybdate, Bi\(_2\)Mo\(_3\)O\(_{12}\), was prepared from an acidic solution (100 ml H\(_2\)O + 69 ml HNO\(_3\)) containing 5.9 g (0.0048 mol) of ammonium heptamolybdate and 10.8 g (0.022 mol) of bismuth nitrate pentahydrate in the presence of 11.7 g (0.056 mol)
of citric acid. After drying (373 K), the powder was calcined in air (1 l min⁻¹), first at 573 K for 20 h, then at 773 K for the same period.

Praseodymium molybdate, Pr₂Mo₃O₁₂, was obtained in an analogous way from solutions containing ammonium heptamolybdate and praseodymium (III) nitrate hexahydrate, corresponding to the stoichiometry of the phase, in the presence of citric acid. The gel obtained after partial removal of water was heated under vacuum at 363 K for 20 h, and then, after grinding, at 1073 K in air for a further period of 20 h.

II.2 Catalysts prepared by the Sol-gel Method

In this section the preparation of all sol-gel dispersed catalysts is described. However it must be noticed that, because the sol-gel process classically refers to the combined use of alkoxides, sections II.2.1 to II.2.6 actually report on the description of catalysts prepared by a mixed co-precipitation method with the assistance of Si(OMe)₄ (TMOS), Mg(OEt)₂ and Al(OiPr)₃.

II.2.1 Preparation of Silica-dispersed Ni-Co molybdates (62)

Adequate amounts of M(NO₃)₂·6H₂O (M = Ni and/or Co) and (NH₄)₆Mo₇O₄₄·4H₂O are dissolved separately in the minimum amount of water in order to obtain final molar ratios corresponding to the following compositions : Ni:Co:Mo 1-x:x:1 (with x = 0, 0.25, 0.50, 0.75 and 1.0). The solutions containing Co and Mo are then added successively dropwise to the Ni solution in order to avoid possible undesired precipitation. When necessary, complete dissolution is ensured by adding some drops of nitric acid. Methanol is then added in order to prevent phase separation when TMOS (tetramethoxysilane) will be introduced later in the medium (TMOS/CH₃OH = 5/3 vol). The slow addition of TMOS (in amounts corresponding to a Si/Mo molar ratio of 5, 10 or 20) is accompanied by an exothermic reaction. Finally, an aqueous solution of 1 wt.% NH₄F (F/Si = 0.01 mol/mol) is added to catalyze the gelation of the catalyst precursor (for major details on the role of NH₄F, see Appendix I.3.1). After gelation (see Appendix II.2 for a list of gelation times), the gels are allowed to age for three weeks before their calcination at a temperature determined from TGA experiments, during 20 hours in a 1 l min⁻¹ of dry air flow. It must be also underlined that the absence of F⁻ ions has been verified by carrying out XPS analyses, and for all catalysts, the result was the same: no trace of F⁻ ions has been detected.
II.2.2 Preparation of Ni(Co)-Ln(Bi)-Mo-Si, Ni-Co-Ln(Bi)-Mo-Si and Ni-Co-Ln-Ln'(Bi)-Mo-Si (Ln, Ln' = La, Ce, Pr, Sm, Tb)

The same starting reagents as described in section II.1.3 are dissolved separately in water in adequate amounts to obtain the following molar composition of the catalysts: Ni(Co)-Ln(Bi)-Mo-Si (1:1:2.5:20), Ni-Co-Ln(Bi)-Mo-Si (1:1:1:2.5:20) and Ni-Co-Ln-Ln'(Bi)-Mo-Si (1:1:1:1:2.5:20). These solutions are slowly added dropwise to each other in order to avoid undesired precipitation. When necessary, complete dissolution is ensured by adding some drops of nitric acid. Methanol is then added (TMOS/CH₃OH = 5/3 vol/vol) in order to prevent phase separation when TMOS will be introduced later in the medium.

Finally, a 1 wt.% aqueous solution of NH₄F (Si/F = 100/1 mol) is added to catalyze the gelation of the catalyst precursor. Generally speaking, usual gelation times of sol-gel prepared Ni or Co molybdates are in the range 2 – 60 min, but in the presence of lanthanides, they increase significantly (see Appendix II.3). In general, the Co-based systems are characterized by shorter gelation times than Ni-based ones. For the preparation of Bi-based catalysts, we operated at low pH values (<1) in order to avoid precipitation of poorly soluble Bi oxosalts produced by hydrolysis. The pH values before gelation of lanthanide-based catalysts lie in the range of 1-3. After gelation, the gels are allowed to age for three weeks before calcination during 20 hours in a 1 l min⁻¹ of dry air flow, at a temperature previously determined from the thermogravimetric experiments.

Different types of thermal degradation schemes are observed for the silica precursor gels. In almost all cases, a progressive weight loss between 573 and 1073 K is observed. The TGA of the Ni(Co)-Ce-Mo-Si (M = Ni, Co) gels exhibit an abrupt degradation in the range 1023-1073 K. Therefore, two different calcination conditions have been selected for the Ni(Co)-Ln(Bi)-Mo-Si systems: 773 K and 1073 K. All other catalysts have been calcined at 773 K for 20 h under a flow of dry air of 1 l min⁻¹.

II.2.3 Preparation of Alumina-dispersed Ni-Co molybdates

Aluminium isopropoxide is dissolved in ethanol at 353 K (Al/EtOH = 0.476 mmol/ml). Separately, adequate amounts of M(NO₃)₂·6H₂O (M = Ni and/or Co) are dissolved in the minimum amount of ethanol in order to obtain final molar ratios corresponding to the following compositions: Ni:Co 1-x:x (with x = 0, 0.25, 0.5, 0.75
These ethanolic solutions are slowly added to the refluxing aluminium isopropoxide. After 30 minutes at a constant temperature of 353 K, some drops of nitric acid and distilled water are added in order to start hydrolysis (H₂O/Al = 0.5 mol/mol, and HNO₃/Al = 1/23.7 mol/mol). An adequate amount of (NH₄)₆Mo₇O₂₄·4H₂O ((Ni+Co)/Mo = 1.0, Al/Mo = 5), is dissolved separately into water (H₂O/Al = 6 mol/mol). After stirring 2 hours, the solution is cooled at room temperature and the aqueous solution of ammonium heptamolybdate is added to this one. The average pH value of the samples before gelation was 6. Gelation occurs within a few minutes in open air. After gelation, the gels are allowed to age for one week, before their calcination at a temperature determined from TGA experiments, during 20 hours in a 1 l/min⁻¹ flow of dry air.

II.2.4 Preparation of Magnesia-dispersed Ni-Co molybdates

Magnesium ethoxide is dissolved in ethanol at 353 K (Mg/EtOH = 1.0 mmol/ml). Separately, adequate amounts of M(NO₃)₂·6H₂O (M = Ni and/or Co) are dissolved in the minimum amount of ethanol in order to obtain final molar ratios corresponding to the following compositions: Ni:Co 1-x:x (with x = 0, 0.25, 0.5, 0.75 and 1.0). After 1 h, these ethanolic solutions are slowly added to the refluxing magnesium ethoxide. An adequate amount of (NH₄)₆Mo₇O₂₄·4H₂O ((Ni+Co)/Mo = 1.0, Mg/Mo = 5) is dissolved separately into water (H₂O/EtOH = 0.29 mol/mol). After stirring 2 hours, the aqueous solution of ammonium heptamolybdate is added to the refluxing solution. After 1.5 hours the solution is cooled at room temperature. The average pH value of the sample before gelation is 8. After gelation, the gels are allowed to age for one week, before their calcination at a temperature determined from TGA experiments, during 20 hours in a 1 l/min⁻¹ flow of dry air.

II.2.5 Preparation of Ni-Co molybdates dispersed on a mixed Al₂O₃-MgO support

Magnesium ethoxide and aluminium isopropoxide are dissolved in a large excess of ethanol (100 ml required + and excess of 50 ml) at 353 K (Mg/EtOH = 1.0 mmol/ml, Al/EtOH = 0.476 mmol/ml)). Separately, adequate amounts of M(NO₃)₂·6H₂O (M = Ni and/or Co) are dissolved in the minimum amount of ethanol in order to obtain final molar ratios corresponding to the following compositions: Ni:Co 1-
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x:x (with x = 0, 0.25, 0.5, 0.75 and 1.0). After 1 h, these ethanolic solutions are slowly added to the refluxing mixed solution of magnesium ethoxide and aluminium isopropoxide. After 1 h, some drops of nitric acid and distilled water are added to 40 ml of ethanol: the resulting solution is then added to the refluxing solution in order to start a pre-hydrolysis (H₂O/Al = 0.5 mol/mol, and HNO₃/Al = 1/23.7 mol/mol). An adequate amount of (NH₄)ₓMo₇O₂₄·4H₂O ((Ni+Co)/Mo = 1.0, (Al + Mg)/Mo = 5, Al/Mg = 2) is dissolved separately into 5 ml water. After stirring for another hour, the aqueous solution of ammonium heptamolybdate is added to the refluxing solution. After 30 minutes the solution is cooled at room temperature. The pH of the samples before gelation was 6. After gelation, the gels are allowed to age for one week, before their calcination at a temperature determined from TGA experiments, during 20 hours in a 1 l/min⁻¹ flow of dry air.

II.2.6 Preparation of Silica-supported α-Bi₂Mo₃O₁₂, β-Bi₂Mo₂O₉ (97) and CeO₂

**Bi-molybdates:** Bi(NO₃)₃·5H₂O and (NH₄)ₓMo₇O₂₄·4H₂O are dissolved separately in the minimum amount of water in order to obtain a final molar ratio Bi/Mo equal to 0.66. The solution containing Mo is then added dropwise to the Bi solution in order to avoid possible undesired precipitation. Complete dissolution is ensured by adding some drops of nitric acid. Methanol is then added in order to prevent phase separation when TMOS will be introduced later in the medium (TMOS/CH₃OH = 5/3 vol). Then TMOS is added in amounts corresponding to a Si/Mo molar ratio of 20. An aqueous solution of 1 wt.% NH₄F (F/Si = 0.01 mol/mol) is added to catalyze the gelation of the catalyst precursor.

After gelation, the gels are allowed to age for three weeks. Calcining the obtained precursor for 20 h under a dry air flow of 1 l min⁻¹ at 773 K led to the formation of the α-Bi₂Mo₃O₁₂. When the precursor was calcined for 20 h at 1073 K, β-Bi₂Mo₂O₉ was formed because of the loss of volatile MoO₃, according to the following reaction:

\[ \text{Bi}_2\text{Mo}_3\text{O}_{12} \rightarrow \text{Bi}_2\text{Mo}_2\text{O}_9 + \text{MoO}_3 \]

**CeO₂:** After dissolving Ce(NO₃)₃·6H₂O in the minimum amount of water, methanol is added, then TMOS is in the amount corresponding to a Si/Ce molar ratio to 20 (TMOS/CH₃OH = 5/3 vol.). An aqueous solution of 1 wt.% NH₄F (F/Si = 0.01 mol/mol) is then added to catalyze the gelation of the catalyst precursor. After aging of
the gel for 3 weeks, the precursor is calcined at 1073 K for 20 h under a dry air flow of 1 l min⁻¹.

II.2.7 Preparation of pure supports by sol-gel method

II.2.7.1 Preparation of Silica

In 6 ml of methanol, 10.2 ml of TMOS are added (TMOS/CH₃OH = 5/3 vol.) and then some drops of nitric acid in order to bring the pH value around 4. An aqueous solution of 1 wt.% NH₄F (F/Si = 0.01 mol/mol) is added to catalyze the gelation of the support precursor, which occurred within one minute. After aging of the gel for 2 weeks, the precursor is calcined at 1073 K for 20 h under a dry air flow of 1 l min⁻¹.

II.2.7.2 Preparation of Alumina (98)

Aluminium isopropoxide is dissolved in 150 ml of ethanol at 353 K (Al/EtOH = 0.476 mmol/ml). After 30 minutes, some drops of nitric acid and distilled water are added in order to start hydrolysis (H₂O/Al = 0.5 mol/mol, HNO₃/Al = 1/23.7 mol/mol, and H₂O/Al = 6 mol/mol). After stirring for 1 hour, the solution is cooled at room temperature and an amount of water equal to the molar ratio (H₂O/Al) = 6 is added to start the gelation process which occurs within a few seconds. Before gelation the pH of the solution is 6-7. The gel is allowed to age one week, before calcination at 773 K during 20 hours in a 1 l.min⁻¹ flow of dry air.

II.2.7.3 Preparation of Magnesia (99)

Magnesium ethoxide is dissolved in 50 ml of ethanol at 353 K (Mg/EtOH = 0.058 mmol/mmol). After 6 hours, an adequate amount of water (H₂O/Mg = 5 mmol/mmol) is added to this solution. After stirring for 1 h, the solution is cooled at room temperature. The pH of magnesia before gelation is 6-7. After gelation, the gel is allowed to age for one week, before its calcination at 773 K, during 20 hours in a 1 l/min⁻¹ flow of dry air.

II.2.7.4 Preparation of Al₂O₃-MgO

Magnesium ethoxide and aluminium isopropoxide are dissolved in a large excess of ethanol (100 ml required + and excess of 50 ml) at 353 K (Al/Mg = 2, Mg/EtOH = 1.0 mmol/ml and Al/EtOH = 0.476 mmol/ml). After 1 h, 40 ml of ethanol containing some drops of nitric acid and distilled water are added to this refluxing
solution in order to start the hydrolysis (H\textsubscript{2}O/Al = 0.5 mol/mol, and HNO\textsubscript{3}/Al = 1/23.7 mol/mol). After one hour, the solution is cooled at room temperature and then 5 ml water are added to start the gelation process. After gelation, the gel is allowed to age for one week, before its calcination at 773 K, during 20 hours in a 1 l min\textsuperscript{-1} flow of dry air.

II.3 Catalysts prepared by Impregnation

The support (Al\textsubscript{2}O\textsubscript{3}, MgO, SiO\textsubscript{2}, TiO\textsubscript{2} and ZrO\textsubscript{2}) was suspended in water. Adequate amounts of M(NO\textsubscript{3})\textsubscript{2}.6H\textsubscript{2}O (M = Ni and/or Co) and (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}.4H\textsubscript{2}O are dissolved in the minimum amount of water in order to obtain final molar ratios corresponding to the following compositions: Ni:Co:Mo 1-x:x:1 (with x = 0, 0.25, 0.5, 0.75 and 1.0). This solution is then added to the suspension of the support in water. After a period of impregnation of 5 hours, the solvent is evaporated by means of a rotary evaporator and then dried during 3 h under reduced pressure. The dry solids are calcined at 773 K for 20 hours under dry air flow of 1 l min\textsuperscript{-1}. The average pH values of the different precursors solutions were: 5 in the case of SiO\textsubscript{2}, 6 for Al\textsubscript{2}O\textsubscript{3}, 8 for MgO and 4 for both TiO\textsubscript{2} and ZrO\textsubscript{2}.

II.4 Pure Phases prepared by the Ceramic Method

La\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12}, La\textsubscript{2}MoO\textsubscript{6}, Sm\textsubscript{2}MoO\textsubscript{6} and Ce\textsubscript{2}Mo\textsubscript{3}O\textsubscript{13} were also prepared by a ceramic route from an intimate mixture of La\textsubscript{2}O\textsubscript{3}, Sm\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2} and MoO\textsubscript{3} engaged with the following molar ratios: (La\textsubscript{2}O\textsubscript{3}/MoO\textsubscript{3}) = 1/3, 1; (Sm\textsubscript{2}O\textsubscript{3}/MoO\textsubscript{3}) = 1 and (CeO\textsubscript{2}/MoO\textsubscript{3}) = 2/3. The mixtures were calcined at 1073 K for 20 h under 1 l min\textsuperscript{-1} of dry air flow, a procedure previously used for the preparation of various Ln\textsubscript{2}MoO\textsubscript{6} compounds (100). The purity of these phases was checked by XRD. The same procedure was also used to prepare Sm\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12}, starting with a mixture Sm\textsubscript{2}O\textsubscript{3}/MoO\textsubscript{3} = 1/3. Although the XRD pattern of this phase did not meet any existing file of Sm-Mo-O phases in the JCPDS database, the diffractogram are perfectly similar those of La\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12} and Pr\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12}, suggesting that this phase corresponds actually to Sm\textsubscript{2}Mo\textsubscript{3}O\textsubscript{12}.
II.5 Description of the analytical techniques

II.5.1 Thermogravimetric analysis (TGA)

The analyses have been performed on a Mettler Toledo TGA/SDTA 851 analyser, in an air flow of 100 ml min\(^{-1}\), from 298 to 1073 K at a heating rate of 10 K min\(^{-1}\). The samples are put in alumina crucibles.

II.5.2 X-ray diffraction (XRD) and X-ray thermodiffractometry

The identification of the crystalline phases was realized by means of X-ray diffraction. Powder X-ray diffraction spectra were measured on a Kristalloflex Siemens D5000 diffractometer using the Cu K\(\alpha\) radiation (\(\lambda = 154.18\) pm). The samples were analysed after deposition on a quartz monocrystal sample-holder supplied by Siemens. The measurements have been made in the 2\(\theta\) range 10° - 80° at a scanning rate of 0.01 degree s\(^{-1}\). The crystalline phases were identified by reference to the powder diffraction data files (JCPDS-ICDD).

X-ray thermodiffractometry was performed with the same apparatus, at a heating rate of 1 K s\(^{-1}\). The temperature was maintained at 303 K for 10 minutes before starting the analysis, then XRD patterns were recorded between 673 and 1073 K, after waiting 1 h at each temperature selected. The temperature was then decreased again to 303 K, at a rate of 10 K s\(^{-1}\) and a final pattern was recorded at 303 K to check the reversibility of the phase transitions.

II.5.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was performed on an SSI-X probe (SX-100/206) spectrometer from FISONS, using the Al-K\(\alpha\) radiation (\(E = 1486.6\) eV) and a hemispherical analyser. The energy scale was calibrated by taking the Au 4f\(_{7/2}\) binding energy at 84 eV. Charge compensation was achieved by the use of a flood gun fixed at 8 eV and a nickel grid at 3 mm above the surface of the samples. The powders were pressed in stainless steel cups (4 mm diameter) and placed on a ceramic sample-holder. The samples were outgassed overnight under vacuum (10\(^{-5}\) Pa) and then introduced into the analysis chamber where the pressure was about 10\(^{-7}\) Pa. The spot size was approximately 1 mm in diameter. The resolution for the general spectra and element spectra was fixed at 4. The binding energies were calculated taking as reference the C-(C,H) component of the C 1s adventitious carbon peak fixed at 284.8 eV. For each
sample, a survey spectrum was recorded, followed by detailed scans of C 1s, O 1s, specific sample elements and finally C 1s again in order to control the charge compensation stability throughout the analysis time.

The analyses of lanthanum, cerium, praseodymium, samarium, bismuth, molybdenum, silicon, aluminium, magnesium, zirconium and titanium were based on the following photopeaks: La 3d5/2, Ce 3d3/2, Pr 3d5/2, Sm 3d5/2, Bi 4f, Mo 3d, Si 2p, Al 2p, Mg 2s, Zr 3d, Ti 2p. Table II.1 lists the constraints applied in the resolution of the XPS spectra.

Table II.1: List of constraints applied in the resolution of the XPS spectra.

<table>
<thead>
<tr>
<th>Elements</th>
<th>∆E</th>
<th>Intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>Mo3d5/2 − Mo3d3/2 = 3.13 eV</td>
<td>I(Mo3d5/2)/I(Mo3d3/2) = 1.50</td>
</tr>
<tr>
<td>Zr</td>
<td>Zr3d5/2 − Zr3d3/2 = 2.43 eV</td>
<td>I(Zr3d5/2)/I(Zr3d3/2) = 1.50</td>
</tr>
<tr>
<td>Pr</td>
<td>Pr3d5/2 − Pr3d3/2 = 20.40 eV</td>
<td>I(Pr3d5/2)/I(Pr3d3/2) = 1.50</td>
</tr>
<tr>
<td>Bi</td>
<td>Bi4f7/2 − Bi 4f7/2 = 5.31 eV</td>
<td>I(Bi4f7/2)/I(Bi4f5/2) = 1.33</td>
</tr>
</tbody>
</table>

For the analysis of the XPS spectra of catalysts in which Ni and La are both involved, the intensity ratio I(La 3d5/2)/I(La 3d3/2) was fixed at 1.50, with an energy difference of 16.78 eV, because of the overlap between Ni2p3/2 and La3d3/2. In the Ni-Ce samples, because of the overlap between the Ni 2p1/2 and Ce 3d5/2 photopeaks, cerium has been quantified by using only the less intense Ce 3d3/2 peak and its satellite. The same procedure was also adopted in Co-Ce-samples to make the comparison easier.

The direct identification by XPS of Tb oxidation state was not possible because of the overlap of the main Tb photopeaks Tb 4d and Tb 4p3/2 with Si 2s and C 1s, respectively.

For the Ni-Co-Mo samples dispersed on different supports (SiO2, Al2O3, MgO, ZrO2, TiO2 and Al2O3-MgO), the analyses of nickel and cobalt were based on the Ni 2p and Co2p photopeaks. In the case of Ni and/or Co molybdates modified by Ln or Bi, the analyses of nickel and cobalt were based on the following peaks: Ni2p3/2 and Co2p3/2 only.

The spectra were decomposed with squares fitting routine with a Gaussian/Lorentzian ratio 85/15 and after subtraction of a calculated baseline (Shirley type). The atomic ratios were calculated by normalizing the surface area ratios with sensitivity factors based on Scofield cross sections.
It is worth reminding that the element ratios measured by XPS can reflect the abundance near the outside surface of catalyst particles, the distribution of elements between the surface layers and the bulk and the degree of dispersion of elements at the surface. However, it must be remembered that the XPS signal of an element present on the surface may be weak if the element is present as relatively large particles.

II.5.4 Raman spectroscopy

Raman spectroscopy was performed on a confocal DILOR-JOBIN-YVON-SPEX spectrometer equipped with a Olympus DX-40. The excitation radiation was a He-Ne laser (632.8 nm) operated at a power of 10 mW. Spectra were obtained by averaging 6 scans of the Raman shift range between 1100 and 100 cm\(^{-1}\) recorded in 60 s with a spectral resolution of 7 cm\(^{-1}\). Some Raman spectra were also recorded on a Renishaw spectrometer (type NIR 780TF Series Laser) at the wavelength of 785 nm. The similarity of the spectra obtained at different places on each sample was systematically verified.

II.5.5 UV-visible diffuse reflectance spectroscopy (UV-Vis DRS)

UV-visible diffuse reflectance spectra were registered on a UV-vis-NIR spectrometer Varian Cary 5E. The samples have been manually ground on a sample-holder and placed in the center of a DRA-C45 integration sphere. Spectra were recorded with background correction in the wavelength range 800 – 200 nm. All results were expressed by Kubelka-Munk units.

II.5.6 Specific surface area measurements (BET), pore size distribution and total pore volume (BJH)

The BET specific surface area measurements were carried out on a Micromeritics ASAP 2000 analyser, using nitrogen or krypton at 77 K. Sample were previously outgassed under vacuum at 473 K. The pore size distribution and total pore volume were determined by using the BJH (desorption) method, assuming a cylindrical pore model.
II.6 Catalytic testing and reaction conditions

Oxidative dehydrogenation of propane to propene (\(\text{C}_3\text{H}_8 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}\)) was carried out in a fixed-bed U-shaped reactor (internal diameter 8 mm) working at atmospheric pressure schematized in fig.II.1. A 4 mm diameter tube introduced into the reactor contains the thermocouple for the temperature control of the catalytic bed. The composition of the gaseous mixture at the reactor output was analyzed with a INTERSMAT IGC 12 M gas chromatograph equipped with two columns: a HAYSEP Q for the separation of propane, propene, CO\(_2\) and water, and MOLECULAR SIEVES for the analysis of oxygen and the detection of CO. Occasionally, this column has been replaced by another one for the detection of acrolein (stationary phase TENAX). Usually carbon monoxide, and rarely acrolein, were found to be side products in the catalytic tests. Helium was used as carrier gas and detection was made by catharometry. The experimental parameters of the chromatographic analyses are shown in table II.2.

<table>
<thead>
<tr>
<th>Table II.2: Experimental parameters of the chromatographic analysis.</th>
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<tbody>
<tr>
<td><strong>Carrier Gas</strong></td>
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<tr>
<td><strong>Column temperature</strong></td>
</tr>
<tr>
<td><strong>Detector temperature</strong></td>
</tr>
<tr>
<td><strong>Injector temperature</strong></td>
</tr>
<tr>
<td><strong>Catharometry current intensity</strong></td>
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</tbody>
</table>

The experiments were conducted with 250 mg catalyst (particle size 315-200 \(\mu\)m), the volume of the catalytic bed being diluted with 250 mg of glass beads (500-800 \(\mu\)m), under the following reaction conditions: volume composition of the reactant mixture: \(\text{C}_3\text{H}_8/\text{O}_2/\text{He}: 10\%: 10\%: 80\%\); total flow rate of 30 ml min\(^{-1}\): this flow rate corresponds to a gas hourly space velocity (GHSV) equal to 4000 h\(^{-1}\). Because the formation of propene by a homogeneous gas phase reaction was observed from above 793 K under the present experimental conditions, the catalytic tests were carried out in temperature range 673 – 753 K. Successive measurements performed during 1.5-2 hours at constant temperature indicated that the catalytic performances remained unchanged over that period of time. Departure from 100 % carbon balance can be due to the formation of coke, CO, acrolein and some other unidentified by-products. In some cases and particularly at the lowest operating temperature (673 K), the carbon balance was
higher than 100 %, because of the low analytical accuracy at very low propane conversion.

Fig.II.1: Oxidative dehydrogenation: set-up for catalytic activity measurements.
II.7 Expression of the catalytic results

The catalytic results will be expressed as propane conversion (XC₃°, %), selectivity in propene (SC₃°, %), propene yield (YC₃°, %), oxygen conversion (XO₂, %), selectivity in CO₂ (SCO₂, %) and CO₂ yield (YCO₂, %). Assuming zero-order reactions as first approximation

*Conversion:*

Reactant conversion (XC₃°, XO₂) is defined as the ratio between the pressure of propane or oxygen converted and the pressure of propane or oxygen introduced and is calculated as follows:

\[
XC₃° = \frac{AC_{3\text{in}} - AC_{3\text{out}}}{AC_{3\text{in}}} \cdot 100; \quad XO₂ = \frac{AO_{2\text{in}} - AO_{2\text{out}}}{AO_{2\text{in}}} \cdot 100
\]

where A is the area of the chromatographic peak.

*Yield:*

The yield in propene represents the ratio of the pressure of propene formed to the initial pressure of propane in the reactor, and it is calculated by:

\[
YC₃° = \frac{AC_{3\text{out}}}{AC_{3\text{in}}} \cdot f_{1,2} \cdot 100;
\]

where f represents the response factor of the gas-chromatograph according to Area = f · Partial Pressure; \( f_{1,2} = fC₃°/fC₃° \); (for calibration curves of C₃H₈, C₃H₆, O₂ and CO₂ see Appendix II.4)

The yield in CO₂ will be tabulated as YCO₂/3 to take into account the formation of three moles of CO₂ per mole of propane converted and to facilitate the comparison with propane conversion:

\[
YCO₂/3 = \left( \frac{ACO_{2\text{out}}}{AC_{3\text{in}}} \cdot f_{3,4} \cdot 100 \right) / 3; \quad \text{where } f_{3,4} = fC₃°/fCO₂;
\]

Because the specific surface areas of the various catalysts are quite different, their performances will be compared on the basis of intrinsic yields in propene and CO₂, noted Y*, the respective yields normalized with respect to the surface area (Y* = Y m⁻², % m⁻²). Occasionally, the intrinsic yield will be expressed in µmol h⁻¹m⁻² considering the following equation: $r(C₃°) = \frac{YC₃° \cdot D}{S_{\text{BET}} \cdot m_{\text{cat}}} \cdot 100$;

where YC₃° represents the propene yield, D, the propane flow (mol h⁻¹), \( S_{\text{BET}} \), the specific surface area of the catalyst (m² g⁻¹) and \( m_{\text{cat}} \), the catalyst mass (g).
The propene productivity has been also calculated and expressed as mmol h$^{-1}$ g$_{ph}$\(^{-1}\) where g$_{ph}$ represents the amount of the active phase dispersed on the support, or as g$_{propene}$ h$^{-1}$ g$_{cat}$\(^{-1}\), where g$_{cat}$ represents the amount of used catalyst.

**Selectivity:**

The selectivity in propene or CO\(_2\) is defined as the ratio between propene yield or CO\(_2\) yield and propane conversion and is expressed in % according to:

\[
\text{SC}_3 = \frac{YC_3}{XC_3} \times 100; \quad \text{SCO}_2 = \frac{(YCO_2/3)}{XC_3} \times 100
\]