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Rationalization of the role played by bismuth and lanthanides in modified Ni–Co molybdates as catalysts for partial and total oxidation of propane

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Abstract

Mixed Ni–Co molybdate catalysts dispersed on silica and modified by Bi or lanthanides (La, Ce, Pr, Sm and Tb) are prepared according to a sol–gel procedure and tested for their activity in propane oxydehydrogenation. Attempts to rationalize the global increase of catalytic activity towards partial and total oxidation are presented, that are based on correlations with fundamental physico-chemical properties of the additional elements: ionization energy, absolute hardness and redox potential. The incorporation of lanthanides in the formulation of these catalysts is shown to allow a fine tuning of the local electronic properties while keeping the same overall oxide lattice structure, due to the similarity of their chemical behaviour and ionic size.

Keywords: Ni–Co molybdates; Partial oxidation; Total oxidation; Bismuth; Lanthanides

1. Introduction

Because the oxidative dehydrogenation (ODH) of light alkanes is a key process to meet the increasing demand for alkenes, new catalyst formulations resulting in higher catalytic performances in this field are definitely welcome. Among the most often cited catalysts for propane ODH, mixed Ni–Co molybdates deserve a particular interest, because of the higher catalytic activity in comparison with simple Ni or Co molybdates [1]. To improve the catalytic behaviour of such catalysts and enhance the alkene productivity in terms of both yield and selectivity, a usual approach consists in incorporating well chosen additional elements in the catalysts formulation. In this work, multicomponent Ni–Co molybdate-type catalysts dispersed in silica are modified by introducing Bi or a lanthanide element, and their catalytic performances are measured in propane ODH.

When several elements are present simultaneously in a multicomponent catalyst with such a complex formulation, attempts can be made to understand how their individual fundamental properties explain the overall catalytic behaviour. The factors determining selectivity in hydrocarbon oxidation and the influence of additives in such catalysts were addressed at several occasions in prominent reviews [2–4]. These considerations derive from the “Mars and van Krevelen” mechanism, which takes into account the activation of the substrate on a metallic cation, the insertion of lattice oxygen and a redox process on the catalyst surface. Within that context, it is common to refer to Haber’s classification of catalytic reactions involving molecular oxygen into two groups: (i) electrophilic oxidations where oxygen is activated into electrophilic species like O_2^- or O^-, leading to total oxidation and (ii) nucleophilic oxidations in which addition of nucleophilic oxygenated species (O^{2-}) favours the formation of partial oxidation products [5]. However, experiments carried out by Del Rosso et al. on α-$NiMoO_4$ without oxygen in the reactor feed showed that lattice oxygen was also responsible for the production of small amounts of CO and CO_2 [6]. To account for the ease of removal of lattice oxygen, different approaches based on several thermodynamic properties were described. In particular, correlations between the redox potential of

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cations present in orthovanadates and their influence on the selectivity for butane ODH were described [7]. A more recent global approach is based on the optical basicity of the oxides, and was applied to a wide series of oxidation reactions [8]. As far as lanthanides are concerned, a correlation between the catalytic properties of binary Ln oxides in butane oxidation and their 4th ionization energy has also been described [9]: the lower the 4th ionization energy, the more active the oxide was in total oxidation. This approach was recently extended to understand the catalytic behaviour of Ln-based binary and ternary oxides in total and selective oxidation of isobutene, either as pure phases or in mixtures with MoO_3 [10]. The correlations were based on various parameters (ionization energy, absolute hardness), accounting for the acid–base and redox properties of all the cations involved.

The purpose of this paper is to look whether the overall catalytic behaviour of complex multicomponent molybdate catalysts in propane ODH can be rationalized using a similar approach. These catalysts correspond to non-stoichiometric compositions resulting in multiphase systems in which a solid solution of Ni–Co molybdates coexists with an excess of MoO_3 and Ln_xO_y, or possibly mixed Ln–Mo–O phases. The objective is to show how differences in yield or selectivity to partial or total oxidation products can be interpreted by referring to fundamental physico-chemical characteristics of the promoting elements that could influence the collective properties of the lattice.

2. Experimental

2.1. Catalysts preparation and characterization

Silica-dispersed mixed Ni–Co molybdates, either pure or modified by Bi or lanthanides (La, Ce, Pr, Sm, Tb) were prepared by a sol–gel method from the metal nitrates, $M(NO_3)_2{\cdot}6H_2O$ (M = Ni, Co), $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = La, Ce, Pr, Sm, Tb), $Bi(NO_3)_3{\cdot}5H_2O$, and ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$. These compounds are dissolved separately in water in adequate amounts to obtain the following molar composition: Ni–Co–Mo–Si 1:1:2.5:20 and Ni–Co–Ln(Bi)–Mo–Si 1:1:1:2.5:20. Methanol is then added ($TMOS/CH_3OH = 5/3$, v/v) in order to prevent phase separation when tetramethoxysilane (TMOS) is introduced later in the medium. Finally, a 1 wt.% aqueous solution of NH_4F ($Si/F = 100/1$ mol) is added to catalyse the gelation of the precursor. After gelation, the gels are allowed to age for 3 weeks before calcination during 20 h in a 1 l min^{-1} of dry air flow at 773 K. The catalysts were characterized by XRD, XPS and Raman spectroscopy.

2.2. Reaction conditions and expression of catalytic results

Oxidative dehydrogenation of propane to propene was carried out in a fixed bed U-shaped reactor. The experiments were performed in the temperature range 673–753 K, using 250 mg catalyst (particle size 315–200 μm) and a reactant mixture with composition (vol.%): $C_3H_8/O_2/He$ of 10:10:80 (total flow rate 30 ml min^{-1}). Catalysts were allowed to equilibrate during 2 h at each measurement temperature before starting the analyses, and were shown to have reached steady-state conditions on the time scale of the experiments. Catalytic results are expressed as propane conversion (XC_3^0, %), selectivity in propene ($SC_3^=$, %), propene yield ($YC_3^=$, %), oxygen conversion (XO_2, %), selectivity in CO_2 (SCO_2, %), and CO_2 yield (YCO_2, %). The conversion is defined as the ratio between the pressure of propane or oxygen converted and the pressure of propane or oxygen introduced. The yield in propene represents the ratio of the pressure of propene formed to the initial pressure of propane in the reactor. The yield in CO_2 will be tabulated as $YCO_2/3$ to take into account the formation of 3 mol CO_2/mol propane converted. The selectivity in propene (CO_2) is defined as the ratio between propene (CO_2) yield and propane conversion ($SC_3^= = YC_3^=/XC_3^0$; $SCO_2 = (YCO_2/3)/XC_3^0$).

3. Results

3.1. Catalysts characterization

The specific surface areas of all catalysts were found to be in the range 280–350 m^2/g. In all samples, XRD revealed the presence of a solid solution of β-$Ni_{0.5}Co_{0.5}MoO_4$ (also confirmed by Raman spectroscopy), sometimes associated with other phases like CeO_2 and $Bi_2Mo_3O_{12}$ in the Bi- and Ce-modified catalysts, respectively. Crystalline MoO_3 has been detected by XRD only in very few cases. According to the XPS analysis, Bi and all lanthanides but Ce are present in their tervalent state at the surface; Ce appears in its (+IV) oxidation state, and we assumed this was also the case for Tb.[1]

3.2. Catalytic performances

Table 1 lists the catalytic performances of all catalysts at 723 and 753 K. The incorporation of La, Ce, Pr and Tb in the catalyst formulation results in improving the catalytic performances of the Ni–Co molybdate catalyst used as reference, by enhancing the overall activity towards partial and total oxidation, and more particularly the propene yield up to a factor 2. In all these cases, the carbon balance is very close to 100% with propene and CO_2 as only products, whereas it amounts to about 75% only in non-modified or Bi-promoted catalysts. The maximum propene productivity is observed at 753 K with the Tb-modified catalyst and corresponds to 0.12 $g_{propene}$ (h g_{cat})$^{-1}$. The catalysts containing Ce or Tb display the highest propane conversions but also the highest

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[1] The direct identification by XPS of Tb oxidation state in the catalyst was not possible because of the overlap of the main Tb photopeaks Tb 4d and Tb $4p_{3/2}$ with Si 2s and C 1s, respectively.

Table 1
Catalytic performances of Ni:Co:Mo:Si and Ni:Co:M:Mo:Si catalysts (M = Bi, La, Ce, Pr, Sm, Tb) in propane ODH

Ni:Co:M:Mo:Si catalysts (M = Ln or Bi)	T (K)	XC_3^0 (%)	$YC_3^=$ (%)	$SC_3^=$ (%)	XO_2 (%)	$YCO_2/3$ (%)	SCO_2 (%)
M = Bi	723	14.5	4.6	31.6	40.8	6.4	43.9
	753	15.2	4.1	26.8	47.8	7.6	49.9
M = La	723	15.5	8.0	51.7	40.3	6.7	42.9
	753	15.9	9.1	57.4	44.3	7.2	45.2
M = Ce	723	20.7	7.1	34.4	88.5	14.0	67.6
	753	22.2	7.9	35.6	96.1	14.1	63.4
M = Pr	723	10.8	6.8	63.3	25.6	4.4	40.5
	753	15.6	9.1	58.3	40.6	6.6	42.1
M = Sm	723	6.8	2.5	37.5	25.6	3.4	50.3
	753	9.2	3.8	40.9	29.8	3.9	42.6
M = Tb	723	21.3	7.4	34.5	62.8	12.2	57.2
	753	26.4	10.0	37.9	74.5	14.3	54.3
M= –	723	6.8	3.5	51.4	13.7	1.7	24.8
	753	11.5	5.4	47.4	22.9	2.8	24.8

selectivity to CO_2. Oxygen consumption is particularly high in the Ce-promoted catalyst. The Bi- and Sm-based catalysts are the least productive systems with respect to propene: the Sm-based catalyst is the least active and the Bi-based catalyst the least selective towards propene. The highest selectivities to propene are obtained in the case of La- and Pr-based catalysts (50–63%).

4. Discussion

When foreign elements are incorporated as dopants in a host oxide lattice, most of its electronic and structural characteristics can in principle be modified: acid–base and redox character, mobility of oxygen, electronic conductivity and vacancies concentration. Furthermore, when several crystalline phases are present simultaneously, additional phenomena related to the interfaces and leading occasionally to phase cooperation can also occur. By referring to our previous approach aimed at rationalizing the role of lanthanides in multiphase catalysts for isobutene oxidation [10], we will present and discuss here three types of correlations based on the concepts of ionization energy, absolute hardness and redox potential (values taken from [11,12]). Although these parameters are interrelated with each other, they reflect different facets of the Lewis acido-basicity and redox character. While redox potential essentially describes the ability to transfer electrons from the catalyst to molecular oxygen, ionization energy is more specifically involved in the M–O bond polarization in the lattice and affects the nucleophilicity of lattice oxygen. The third parameter, absolute hardness, which is a combination of IE and electron affinity, is involved in the overall catalytic process, by allowing to describe the interactions between catalyst, substrate and intermediate products on the basis of preferential hard–hard interactions.

4.1. Ionization energy

Fig. 1 shows the evolution of CO_2 yields (%) with respect to the ionization energy (IE); considering the major

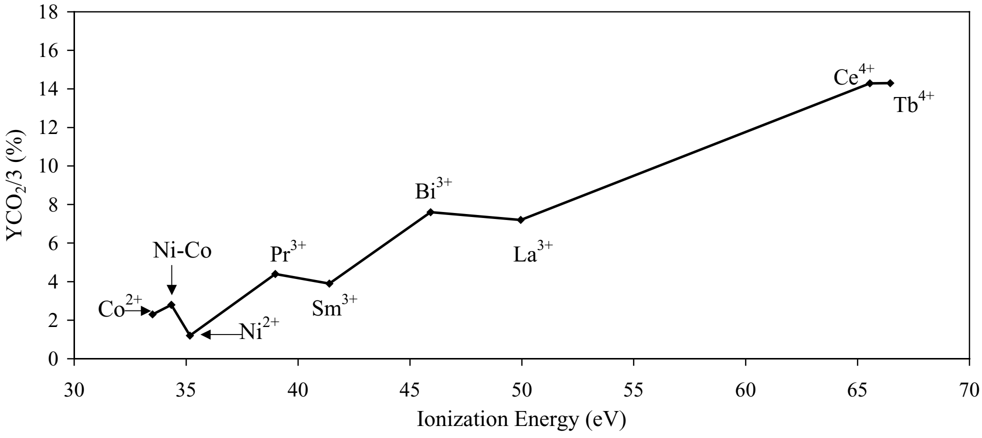

Fig. 1. Evolution of the CO_2 yield (T = 753 K) with respect to the ionization energy.

oxidation state identified by XPS or assumed (Tb, see Section 3.1) at the catalyst surface, this graph refers to the 4th IE ($Ln^{3+} \rightarrow Ln^{4+}$) for Bi, La, Pr and Sm, whereas the 5th IE ($Ln^{4+} \rightarrow Ln^{5+}$) is used for Ce and Tb. Fig. 1 shows that the most active catalysts towards total oxidation are those characterized by an additional element with the highest IE. This trend is actually the opposite of that found previously, on the basis of the 4th IE values only, when binary oxides Ln_xO_y were used in total or selective oxidation of butane [9] or isobutene [10]. In those two cases, the tendency to total oxidation was higher with oxides containing elements with low 4th IE values, in line with the fact that this would facilitate the formation and increase the concentration of surface electrophilic oxygen species resulting from electron transfers between M^{n+} cations and adsorbed molecular oxygen (O^{2-}, $O_2{}^{2-}$, O^-). The fact that reverse behaviours are observed suggests that, even if a Mars and van Krevelen-type mechanism is accepted with the first hydrogen-abstraction from the secondary C–H bond being the rate-determining step [13], some key mechanistic features could actually differ. The observation of low CO_2 yields in the presence of elements with low IE values suggests that in this case the metal cation is essentially involved through its neighbourhood with lattice oxygens whose nucleophilicity increases when the metal IE decreases. In comparison with the non-modified Ni, Co or Ni–Co molybdate catalysts used as references, the incorporation of Bi^{3+} or $Ln^{3+/4+}$ in the molybdate lattice affects the polarization of the M^{n+}–O^{2-} and consequently the electron density on the lattice O^{2-} anions. Different properties can therefore be expected according to the way these elements are distributed in the lattice, namely the various possible arrangements like the $Ni^{2+}(Co^{2+})$–O^{2-}–Mo^{VI} and $Ln^{3+/4+}(Bi^{3+})$–O^{2-}–Mo^{VI} moieties. In the presence of additional elements with low IE, the average nucleophilicity of lattice oxygen will increase and lower CO_2 yields result. In this way, the global evolution of the CO_2 yield with respect to the IE values seems to account quite satisfactorily for the influence of the additional elements.

4.2. Absolute hardness

A second correlation can be described between the catalytic performances and the Lewis acid–base properties of the cations involved, which can be represented by their absolute hardness. While coordinatively unsaturated metallic ions in a high oxidation state can be considered as acidic centres, oxygenated ions and organic substrates constitute basic centres. For propane ODH, it is usually claimed that the catalysts have to display a certain hard acid character to activate propane, which is assimilated to a poorly polarizable, hard base, due to the presence of strong σ bonds. In Fig. 2, propane conversion, CO_2 yields and selectivity to propene at 753 K are plotted against the absolute hardness of the concerned ions, calculated according to Pearson's definition. A similar bell-shaped relationship appears for the propane conversion and the yield in CO_2, with a maximum occurring for Ce^{4+} and Tb^{4+}. On one hand, the initial increase of propane conversion and CO_2 yield with increasing hardness reflects the importance of strong interactions between the alkane and the metal cation to activate the substrate (rate-determining step) and convert it into total oxidation products. This fact is in line with HSAB concepts, on the basis that the oxidation of an alkane would be more selective if it involves a soft cation rather than a hard one, because the interaction with the catalyst would be weaker. On the other hand, decrease of these parameters at high hardness values reflects the necessity to have well-adjusted acid–base properties between the alkane and the catalyst. For very hard cations (La^{3+}), the increase in selectivity to partial oxidation could also be the consequence of much weaker interactions between the catalyst and the formed propene, which would desorb more easily from the surface.

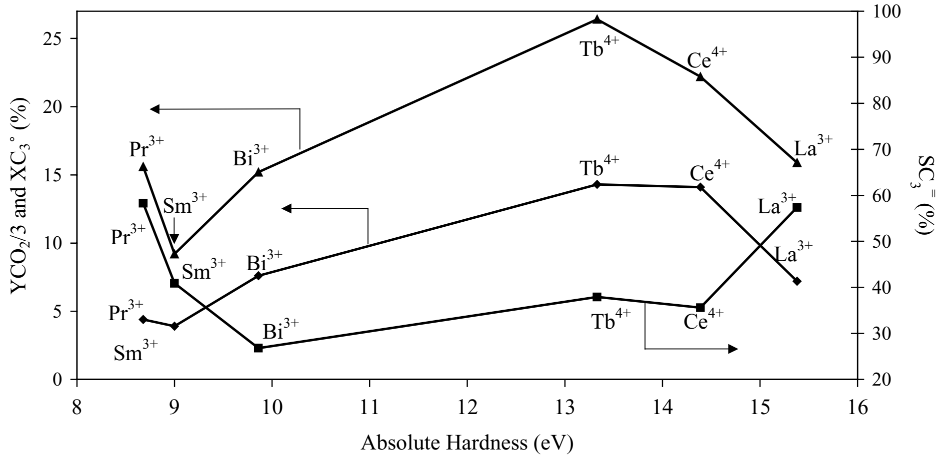

Fig. 2. Evolution of the CO_2 yield (◆), propane conversion (▲) and the selectivity to propene (■) with respect to the absolute hardness of the additional elements (data at $T = 753$ K).

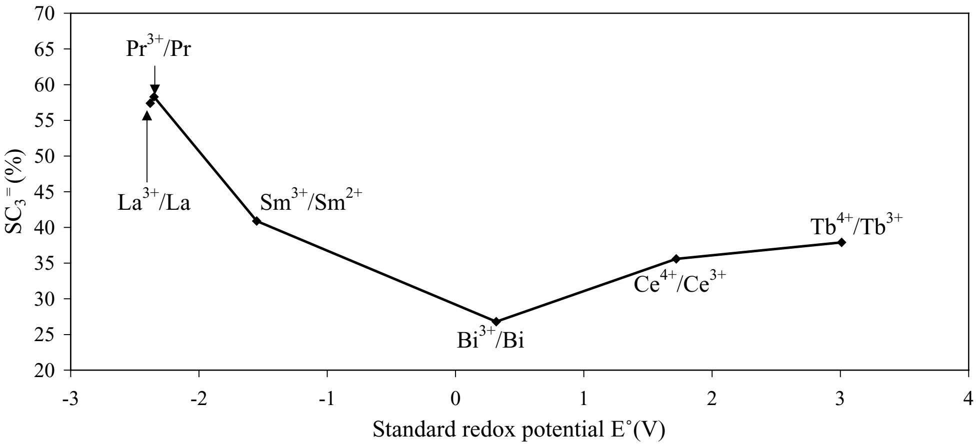

Fig. 3. Evolution of the selectivity to propene ($T = 753\,\mathrm{K}$) with respect to the standard redox potential of the additional elements.

4.3. Redox potential

Fig. 3 illustrates a third correlation between selectivity to propene and the standard redox potential of the additional elements. The most selective catalysts are characterized by the lowest redox potentials. In this case, the low reducibility of the M^{n+} cation diminishes the availability of lattice oxygen (O^{2-}) as electrophilic species (like O^-), promoting thereby partial oxidation. On the other hand, the relatively higher selectivities reached in the case of Ce^{4+} and Tb^{4+} could be explained by the involvement of Ln^{4+}/Ln^{3+} redox couples: on one hand, the high reducibility of Ln^{4+} species would in principle favour total oxidation (the absolute CO_2 yields are high) by facilitating the conversion of O^{2-} to O^-, but on the other hand, the resulting steady-state concentrations of reduced Ln^{3+} species could be involved in the reoxidation mechanism of the reduced catalyst and permit fast replenishment of the lattice oxygen vacancies by helping to convert molecular oxygen to O^{2-} species.

5. Conclusions

This work on the use of silica-dispersed mixed Ni–Co molybdate catalysts modified by different elements in propane ODH demonstrates the interest of incorporating lanthanides in the lattice to improve the overall catalytic behaviour, in terms of activity and selectivity to propene. The correlations described between the propane conversion, 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, suggest that these parameters are useful theoretical tools to account for the global properties of multicomponent oxidation catalysts involving several active elements. In particular, it 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 favours the substitutional incorporation in the oxide lattice.

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