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Acid–Base Properties of Metallic Oxide Catalysts studied by Conversion of Propan-2-ol

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Conversion of propan-2-ol in the absence of air has been used to characterize the acid–base properties of metallic oxides. Two families of solids were studied: the first, niobic acid and oxides exhibited only acidic properties, *i.e.* resulted only in formation of propene, the second, mixed cobalt and nickel molybdates in their α or β forms, exhibited acidic and basic properties *i.e.* resulted in the formation of both propene and acetone. It was also observed that β-phase molybdates are more active and slightly more selective for propene than the α-phase molybdates.

Propan-2-ol conversion to propene (acid catalysed) and/or acetone (redox or acid–base catalysed) is widely used to characterize acid–base or redox properties of catalysts.[1–10] Kinetics and mechanistic studies are usually necessary to determine which types of catalytic sites are involved. For propene formation, three mechanisms are considered, namely E_1 (Brønsted H^+ site), E_2 (acid–base pair site) and concerted E_{1cB} (acid–base pair site).[9–14] For acetone formation, two mechanisms are invoked, the first with an alkoxy intermediate and the abstraction of the H on C_α as the limiting step[15–17] and the second with the formation of an enolate intermediate and the abstraction of an H on C_β as the limiting step.[18]

Niobic acid is known to be a rather strong acid whose acidity decreases on transformation to Nb^V oxide.[19] Only propan-2-ol conversion to propene was studied in our work to characterize changes in acidic features during this transformation.

$CoMoO_4$ and $NiMoO_4$ are isostructural molybdates which form solid solutions over the whole concentration range. They are known for their effect on propene oxidation (partial oxidation to acrolein and to acrylic acid, respectively). Conversion of propan-2-ol to propene and acetone was used in this work to characterize the effect of Co^{2+} substitution for Ni^{2+} on the acid–base properties (in the absence of air) and redox properties (in the presence of air).

Experimental

Niobic acid was prepared in the laboratory by hydrolysis of $NbCl_5$ (Aldrich 99%) in aqueous solution by NH_4OH at pH 7. After filtration and washing with ion-exchanged water, the sample was dried at 383 K.

Cobalt molybdate and mixed $Co_{1-x}Ni_xMoO_4$ samples were prepared by Ponceblanc[20] by coprecipitation of cobalt nitrate and nickel nitrate with ammonium heptamolybdate at pH 8, adjusted by NH_4OH solution. After filtration and washing with ion-exchanged water, the samples were calcined for 15 h at 773 K in order to obtain the β form. X-Ray diffraction analyses confirmed that the solids obtained were solid solutions in the β form.

Chemical analyses by atomic absorption, BET surface-area measurements (*t* method) and X-ray diffraction experiments (using a Siemens K 710 X-ray source and a Phillips PW 1710 goniometer with a Cu cathode) were performed in our laboratory. Differential thermal analysis (DTA) was performed with a Setaram MTD 85 equipment under a flow of N_2 or Ar.

Catalytic conversion of propan-2-ol was carried out in a differential-flow microreactor (0.2 to 1.0 g of catalyst) attached to an on-line gas chromatography apparatus (flame ionization detector and catharometer). Propan-2-ol was introduced in a range of pressures from 0 to 4 kPa with N_2 as a carrier gas and a total flow rate varying from 15 to 60 cm^3 min^{-1}. The catalytic results are expressed as intrinsic rates of propene and acetone formation.

Results and Discussion

Nb^V oxides

Niobic acid is an isopolyacid $H_8Nb_6O_{19} \cdot xH_2O$ that is known to exhibit strong acidity because of its very labile protons.[19] The samples were calcined at increasing temperatures from 373 to 773 K under N_2 flow and then cooled to the reaction temperature under N_2. Their designation and some of their characteristics are given in Table 1.

The initial sample was shown by XRD to be amorphous but some peaks of γ-Nb_2O_5 appeared after calcination at 773 K.

DTA showed two endothermic peaks at 398 and 473 K due, respectively, to the elimination of adsorbed and crystallization water molecules and an exothermic peak at 848 K which, according to ref. 5, is due to the crystallization of the γ

Table 1 Characteristics of $Nb_2O_5 \cdot xH_2O$ samples

samples	calcination temperature /K	surface area /m^2 g^{-1}	total acid sites[a] /10^{-7} mol m^{-2}	initial differential heat[a]/ kJ mol^{-1}	rate of propene formation[b] /10^{-10} mol s^{-1} m^{-2}
A_1	373	140	—	—	1.1
A_2	473	104	27.5	160	1.0
A_3	573	86	25.7	196	1.2
A_4	673	64	28.1	168	1.3
A_5	773	35	11.4	86	0.4

[a] Determined by microcalorimetry of NH_3 adsorption, at 373 K, from ref. 11. [b] Rate of propene conversion at 423 K with $P_i = 2$ kPa and total flow rate = 30 cm^3 min^{-1} in the absence of oxygen.

phase. Thermogravimetric analysis showed that there was a weight loss of 5.7% and 1.8% for samples A_1 and A_3, respectively, on heating to 400 °C, corresponding to the following formulae: $Nb_2O_5 \cdot 0.9H_2O$, *i.e.* $0.33Nb_2O_5 \cdot 0.23H_8Nb_6O_{19}$, $Nb_2O_5 \cdot 0.26H_2O$, *i.e.* $0.90Nb_2O_5 \cdot 0.03H_8Nb_6O_{19}$.

The acid properties of the samples were determined by microcalorimetry of NH_3 adsorption at 373 K.[11] It appears clearly from Table 1 that the total concentration of acid sites was roughly constant up to a calcination temperature of 673 K and decreased sharply above it.

The catalytic studies were conducted in a non-diffusional regime, in the temperature range 403 to 473 K in order to maintain the conversion level at less than 8%. During the first 2 h, only a slight deactivation (<10%) was observed with time on stream while selectivity to acetone decreased from 3 to 0%, the other product being propene. The dependence of the rate of propene formation on the partial pressure of propan-2-ol and on the temperature was studied in steady-state conditions on sample A_3, with a total flow rate of 30 $cm^3\ min^{-1}$ and catalyst mass 0.5 g. In Fig. 1, the rate, r_p, of propene formation is plotted against the partial pressure of propan-2-ol (P_i), at various temperatures. It is observed that the reaction order varies from 1 at low pressures to 0 at high pressures. Plotting $1/r_p$ *vs.* $1/P_i$ led to a set of straight lines (Fig. 2) showing that the rates of propene formation obeys the Langmuir–Hinshelwood equation:

$$r_p = k_p \lambda_i P_i/(1 + \lambda_i P_i) \qquad (1)$$

where k_p is the rate constant and λ_i, the equilibrium constant for adsorption of propan-2-ol. k_p and λ_i are calculated from the slopes and intercepts of the straight lines for various reaction temperatures (Table 2) and from an Arrhenius plot the true activation energy and the heat of adsorption for propan-2-ol were calculated to be 108 ± 6 kJ ml^{-1} and 98 ± 6 kJ mol^{-1}, respectively.

This value of the true activation energy was checked using a random programme of temperatures under the following conditions: $P_i = 2$ kPa, flow rate = 30 $cm^3\ min^{-1}$, catalyst mass = 0.1 g, *i.e.* in conditions of zero-order. The value obtained from the Arrhenius plots was 104 ± 6 kJ mol^{-1}.

An inhibiting effect of water was observed when the partial pressure of water added in the feed varied from 0 to 2.4 kPa (Fig. 3). This may be attributed to competitive adsorption of propan-2-ol and water resulting in a decrease in the number of active sites. This also shows that the new Brønsted sites were not formed by hydrating Lewis sites in the presence of water in the feed.

In the presence of oxygen in the feed ($P_{O_2} = 19.3$ kPa), the rates of propene formation, which remained constant with time on stream, corresponded to the initial rates observed in the presence of N_2 as carrier gas. Acetone was also formed but with a very low selectivity of *ca.* 1%. The activation energy for the propene formation was unchanged: 104 ± 6 kJ mol^{-1} and that for acetone formation was 75 ± 6 kJ mol^{-1}. These results show that the active sites for the formation of acetone are rapidly deactivated in the absence of oxygen, but not in its presence, and that they are present in much lower amount than the acid sites. The presence of oxygen in the feed has no influence on the mechanism of the dehydration to propene and it only reduces its deactivation with time on stream.

The kinetics study allows us to conclude that the superficial reaction constitutes the limiting step (adsorption–desorption steps are near the equilibrium), that justifies its use in the characterization of the superficial properties of catalysts.

The influence of the precalcination temperatures of the samples on the rate of propene formation was measured at

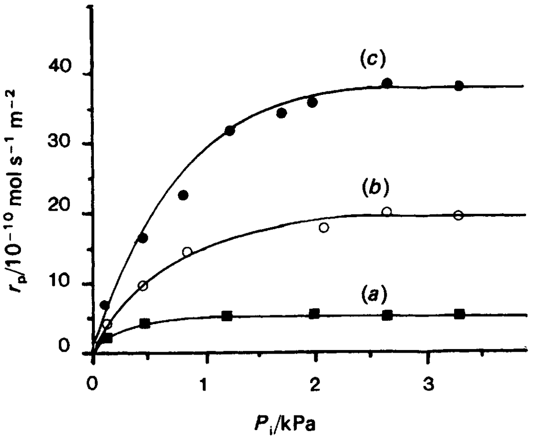

Fig. 1 Variations of the intrinsic rate of propene formation on $Nb_2O_5 \cdot xH_2O$, A_3 sample, *vs.* propan-2-ol partial pressure at (*a*) 415, (*b*) 436 and (*c*) 447 K. Total flow rate = 30 $cm^3\ min^{-1}$, catalyst weight = 0.5 g.

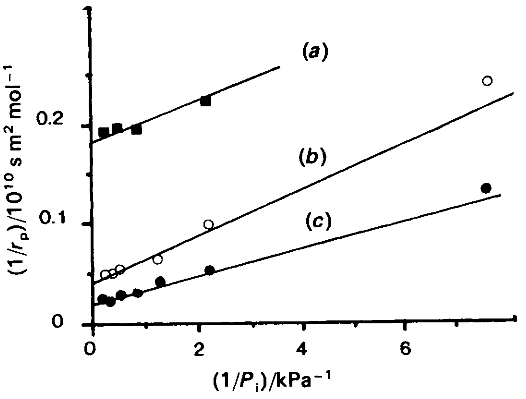

Fig. 2 Plots of $1/r_p$ *vs.* $1/P_i$ at: (*a*) 415, (*b*) 436 and (*c*) 447 K for sample A_3

Table 2 Values of the kinetic constants

reaction temperature /K	k_p /10^{-10} mol s^{-1} m^{-2}	λ_i/ 10^{-3} Pa^{-1}
415	5.4 ± 0.2	9.5
436	22 ± 2	2.5
447	45 ± 3	1.3

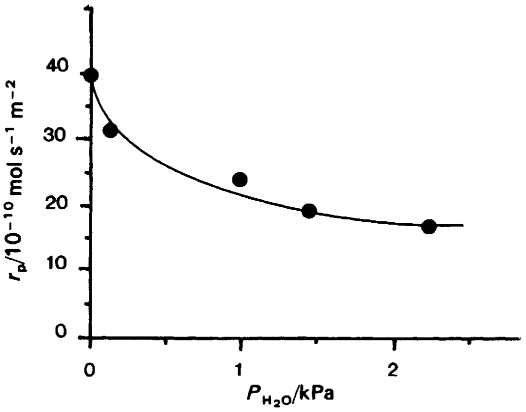

Fig. 3 Inhibiting effect of H_2O in the feed for sample A_3. Total flow rate = 30 $cm^3\ min^{-1}$, catalyst weight = 0.5 g, $P_i = 1.7$ kPa, reaction temperature = 447 K.

423 K with a partial pressure of propan-2-ol of 2 kPa, *i.e.*, in zero-order with respect to P_i. It was observed (see Table 1) that the reaction rate increased slightly with the calcination temperature up to 673 K and decreased sharply at higher temperatures. This characterizes the change in acidic features and is similar to the results determined by microcalorimetric measurements[11] and as described by Tanabe in Fig. 5 of ref. 19. It can be concluded that the rate of propene formation depends on the total number of acid sites.

Mixed Cobalt–Nickel Molybdates

The isotypic molybdates $MMoO_4$, where M = Co, Fe or Ni, exist in two polymorphous forms: α and β. At room temperature, the stability or metastability of these phases depends on the nature of the cation M. For example, $CoMoO_4$ corresponds to a mixture of α phase (stable form) and β phase (metastable form) while for $NiMoO_4$ only the α phase is present. Because of the isomorphism of these molybdates and the similar value of the ionic radii of Co and Ni cations, $Co_{1-x}Ni_xMoO_4$ solid solutions exist over the whole composition range.[20]

First we carried out a kinetics study of β-$CoMoO_4$ at steady-state conditions that were reached after 1 or 2 h on stream and corresponded only to 20% loss in activity. Both propene and acetone were detected, even in the absence of oxygen, but at temperatures ranging from 473 to 513 K, *i.e.* at a much higher temperature than for Nb^V oxide.

The reaction orders for propene and acetone formation *vs.* the partial pressure of propan-2-ol varied from 1 to 0 and, as observed for Nb^V oxides, linear relations between $1/r_p$ or $1/r_a$ and $1/P_i$ were found (Fig. 4). Again, the results may be interpreted in terms of a Langmuir–Hinshelwood type reaction with two independent sites for propan-2-ol adsorption, one leading to propene, the other to acetone:

$$r_p = k_p \lambda_p P_i/(1 + \lambda_p P_i) \quad \text{and} \quad r_a = k_a \lambda_a P_i/(1 + \lambda_a P_i)$$

where p and a subscripts refer to propene and acetone respectively.

In the temperature range from 473 to 513 K, the true activation energies for propene and acetone were calculated from the Arrhenius diagrams obtained using the random programme of temperature under zero-order conditions. They are 125 ± 6 kJ mol^{-1} for propene and 100 ± 6 kJ mol^{-1} for acetone.

It was observed that water in the feed had an inhibiting effect for propene formation but not for acetone. The Arrhenius diagrams show that in presence of 0.29 kPa of water the activation energy values remained constant for acetone and increased from 125 to 165 kJ mol^{-1} for propene. This confirms that the sites responsible for the two reactions are independent.

When oxygen was introduced in the feed at various partial pressures varying from 0 to 40 kPa (Fig. 5), it was observed that the rate of propene formation remained approximately constant whilst that of acetone increased by a factor of three. Moreover, the true activation energy (determined in zero-order *vs.* propan-2-ol and oxygen) was unaffected for propene formation and decreased to roughly 65 kJ mol^{-1} for acetone formation (Fig. 6).

These results support our conclusion that propene and acetone are formed on two independent sites. The sites responsible for propene formation are inhibited by water (as already observed for $Nb_2O_5 \cdot xH_2O$) and remained unchanged in the presence of oxygen. The acid–base pairs responsible for acetone formation are strongly activated in the presence of oxygen which indicates that they are related to redox properties of the material.

As for $Nb_2O_5 \cdot xH_2O$, we have determined the acidic properties of $CoMoO_4$ by microcalorimetry of NH_3 adsorption at 373 K. The same characteristics[11] for samples A_1 to

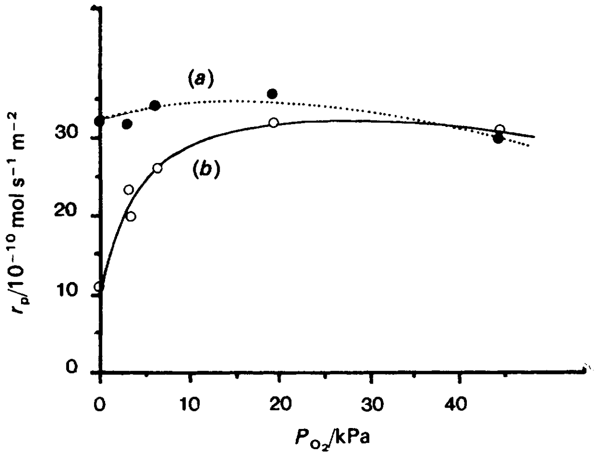

Fig. 5 Influence of oxygen pressure on the intrinsic rates of (*a*) propene and (*b*) acetone formation on the β-$CoMoO_4$ sample. Total flow rate = 47 cm^3 min^{-1}, catalyst weight = 0.2 g, P_i = 2.9 kPa, reaction temperature = 503 K.

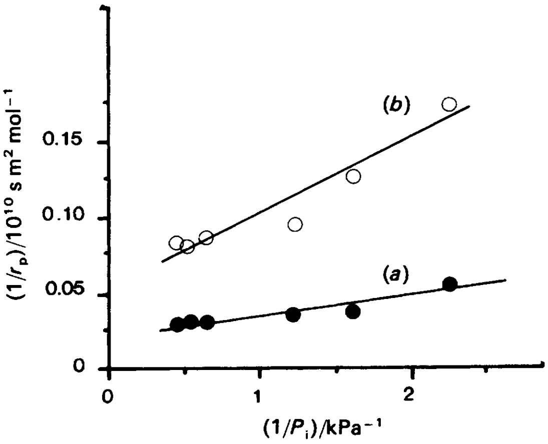

Fig. 4 Plots of $1/r_p$ *vs.* $1/P_i$, (*a*) propene formation, (*b*) acetone formation, for β-$CoMoO_4$ at 502 K. Total flow rate = 30 cm^3 min^{-1}, catalyst weight = 0.2 g.

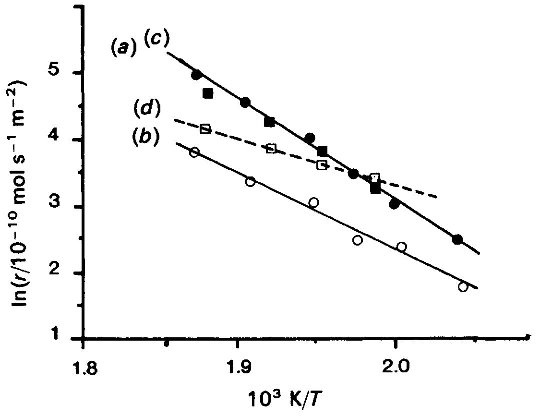

Fig. 6 Arrhenius diagrams obtained for β-$CoMoO_4$ samples, in the absence of oxygen for (*a*) propene formation, (*b*) acetone formation and in the presence of 44.7 kPa oxygen for (*c*) propene formation, (*d*) acetone formation. Total flow rate = 47 cm^3 min^{-1}, catalyst weight = 0.2 g, P_i = 2.9 kPa.

Table 3 Characteristics of β-$Co_{1-x}Ni_xMoO_4$ catalysts (from ref. 20)

sample	Ni/(Ni + Co) (at.%)	surface area /m^2 g^{-1}	rate of formation[a]/ 10^{-10} mol s^{-1} m^{-2}	
			propene	acetone
$CoMoO_4$	0	27.0	0.01	1.09
CNM_1	2	9.5	3.36	2.82
CNM_2	6	29.5	4.27	3.64
CNM_3	12	37.5	4.64	1.55
CNM_4	19	32.5	2.18	1.91
CNM_5	40	37.0	0.55	0.76
$NiMoO_4$	100	53.5	0.64	1.09

[a] Rates were measured at 423 K in the absence of air.

A_4 were observed, *i.e.* a total concentration in acidic sites corresponding to 27×10^{-7} mol m^{-2} and an initial differential heat of adsorption of 170 kJ mol^{-1}.

Comparison with the catalytic data obtained for niobic acid leads to the following remarks:

(1) The rate constant of propene formation, k_p, at 423 K is 1.2×10^{-10} mol m^{-2} s^{-1} for $Nb_2O_5 \cdot xH_2O$ (sample A_3) and 0.18×10^{-10} mol m^{-2} s^{-1} (obtained by extrapolation at 423 K) for β-$CoMoO_4$ while the number and strength of acid sites, as measured by microcalorimetry of NH_3 adsorption, are very close.

(2) The activation energy value for propene formation is much higher for β-$CoMoO_4$ than for niobic oxide (125 and 108 kJ mol^{-1}, respectively). This means that the mechanism is different probably owing to the difference in nature of acid sites, probably cations in the former case and protons in the latter.

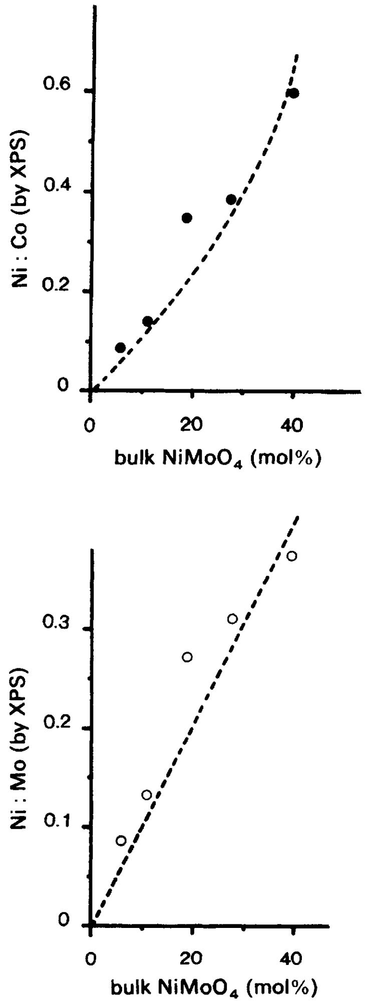

Fig. 7 XPS results expressed as atomic ratios *vs.* chemical analysis for β-$Co_{1-x}Ni_xMoO_4$ samples

The results on activities and activation energy values compared with microcalorimetry results show that for catalysts of different nature, propene formation is more related to the nature (*i.e.* Brønsted or Lewis acid) of the sites than to their acidic strength and concentration.

(3) The difference in true activation energy values for propene and acetone shows that comparison between samples exhibiting very different activities is difficult since the reaction temperature affects considerably the relative rates of acetone and propene formations. Thus, the selectivity being temperature dependent cannot be used to calculate a number of basic sites as proposed in ref. 21 and 22. However, comparison of samples at the same reaction temperature may give information on the variations of their acid and basic properties.

Secondly the catalytic behaviour of the mixed molybdates β-$Co_{1-x}Ni_xMoO_4$ which are solid solutions, was studied. The activity of β-$CoMoO_4$ was considerably enhanced by the presence of Ni^{2+} in the lattice and so catalytic studies on the mixed molybdates were carried out at temperatures ranging from 423 to 473 K to keep a low conversion level. However, kinetics studies at the steady state led to the same Langmuir–Hinshelwood equation for the rates of propene and acetone formation. Moreover, the true activation energy values calculated from Arrhenius plots over the whole range of Ni composition were constant and of the same order as

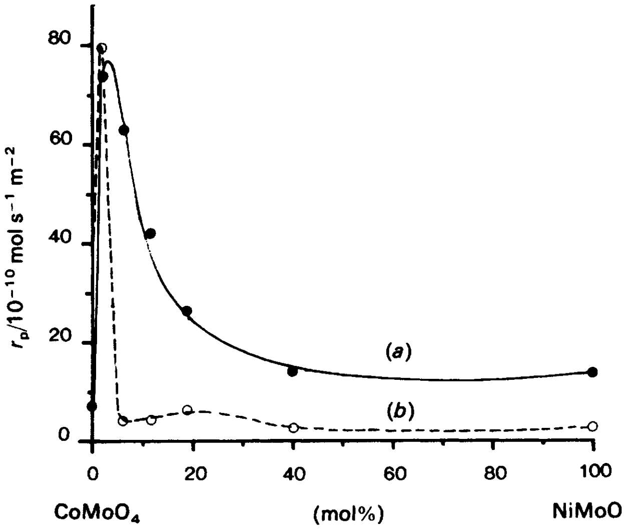

Fig. 8 Intrinsic rates of (*a*) propene formation and (*b*) acetone formation on β-$Co_{1-x}Ni_xMoO_4$ samples. Total flow rate = 30 cm^3 min^{-1}, catalyst weight = 0.2 g, P_i = 3.2 kPa, reaction temperature = 458 K.

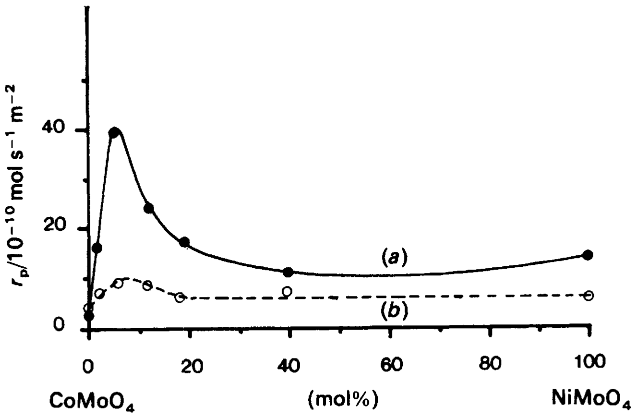

Fig. 9 Intrinsic rates of (*a*) propene formation and (*b*) acetone formation on α-$Co_{1-x}Ni_xMoO_4$ samples. Total flow rate = 30 cm^3 min^{-1}, catalyst weight = 0.2 g, $P_i = 3.2$ kPa, reaction temperature = 458 K.

for β-$CoMoO_4$: $E_p = 110$–130 kJ mol^{-1} and $E_a = 75$–85 kJ mol^{-1}.

The variations in the rates of propene and acetone formation, at 423 K, *vs.* Ni content, are reported in Table 3. It is worth noting that a particular enhancement occurs between 2 and 20 at.% Ni for both propene and acetone but particularly for propene.

X-Ray photoelectron spectroscopy (XPS) (Fig. 7) showed that for such samples the superficial composition of the crystallites was very similar to that of the bulk except for the CNM_1 sample for which no Ni was detected, but this may be due to a lack of sensitivity. At present, in the absence of any modification detectable by our techniques such as IR, XRD and XPS, this phenomenon may be considered as a synergy effect like those observed with many mixed oxides and particularly with mixed molybdates.[23–25]

In order to determine if the transition $\alpha \rightarrow \beta$ changes the catalytic properties of these materials, the same study was carried out on α-$Co_{1-x}Ni_xMoO_4$ obtained by grinding the β mixed molybdate sample at room temperature. The transition was evidenced by the colour change from purple to green and by XRD. Because of the lower activity of the α phase, the catalytic performances were measured at 458 K. In Fig. 8 and 9, the propene and acetone rates were plotted *vs.* Ni content for the α and β phases, respectively. As previously reported, a catalytic enhancement was observed between 2 and 20% Ni, particularly for propene formation. In the same range of compositions, the α-phase samples were less active than the β ones, particularly for propene formation, as shown in Fig. 7 and 8, *i.e.* these α-phase samples exhibited weaker acidic properties than the β ones. The activity and selectivity for the $NiMoO_4$ sample did not change after grinding which confirms that the only stable phase for this molybdate is α. These results when compared with those given in Table 3 (data at 423 K) evidenced a gain of selectivity to propene with temperature, in good agreement with the values of the activation energies.

Conclusions

Propan-2-ol conversion into propene and acetone in the absence of air is an interesting test reaction for characterizing acidic, acid–base and redox properties of metallic oxides. Nevertheless, it is difficult to apply this method reliably because different sites and different mechanisms may be involved. In particular, comparison of relative rates of propene and acetone formation for determining amounts of acidic and basic sites may not be valid since it depends strongly on the respective activation energy values, *i.e.* on the temperature of reaction, propene being always favoured at high temperatures. Moreover, propene formation appears to be very sensitive to the nature of the acid sites (Brønsted or Lewis types) while the microcalorimetry technique of NH_3 adsorption is sensitive to the strength and concentration but not to the nature of the sites.

Niobic acid has Brønsted acid sites giving only propene formation upon propan-2-ol conversion and the acidity remains nearly constant with calcination temperature up to 673 K where formation of niobic oxide and thus of Lewis-type acid sites occurs.

α-Ni molybdate is found to be more active and particularly more acidic than α-Co molybdate. It may be suggested that both molybdates exhibit acid–base pair sites of similar (strength) or amount and very probably of Lewis type.

When Ni is incorporated into Co molybdate, a solid solution is formed resulting, at low Ni content (<20 mol%), in enhanced propene formation, *i.e.* in enhanced acidic features. Moreover, but to a lesser extent in the same Ni range, acetone formation is enhanced, *i.e.* new acid–base pair and redox sites are also formed. The same tendencies are observed for both α and β phases although the α phase molybdates are less active and less selective for propene.

At present, we are unable to relate this synergy effect to any physicochemical property, characterized in this work, which shows that a catalytic reaction is a more sensitive tool than the other methods of characterization we have used.

References

1 P. Sabatier and L. Maihle, *Ann. Chim. Phys.*, 1910, **20**, 289.
2 K. Tanabe, *Solid Acids and Bases*, Kodansha, Tokyo, 1970.
3 K. Tanabe, M. Misono, Y. Ono and H. Hattori, *Stud. Surf. Sci. Catal.*, 1989, **51**.
4 M. E. Winfield, in *Catalysis*, ed. P. H. Emmett, Waverly Press, Baltimore, 1960, vol. VII, p. 93.
5 H. Pines and J. Manassen, *Adv. Catal.*, 1966, **19**, 49.
6 J. M. Winterbottom, *Catalysis*, Royal Society of Chemistry, London, 1981, vol. 4, p. 141.
7 M. Ai, *J. Catal.*, 1975, **40**, 327; 1977, **49**, 305.
8 B. Grybowska-Swierkosz, *Mater. Chem. Phys.*, 1987, **17**, 121.
9 F. Figueras-Rocca, L. de Mourgues and Y. Trambouze, *J. Catal.*, 1969, **14**, 107.
10 A. Nohl, Ph.D. Thesis, University of Lyon, France, 1970, no. 646.
11 A. Ouqour, Ph.D. Thesis, University of Lyon, France, 1991, no. 105-91.
12 H. Vinek, H. Noller, M. Ebel and K. Schwarz, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 734.
13 H. Knözinger and A. Scheglila, *J. Catal.*, 1970, **17**, 252.
14 Y. Imuzi, T. Yamaguchi, H. Hattori and K. Tanabe, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1040.
15 H. Niyama and E. Echigoya, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1739.
16 L. Nondek and J. Sedlacek, *J. Catal.*, 1975, **40**, 34.
17 N. Takezawa, C. Hanamaki and H. Kobayashi, *J. Catal.*, 1974, **34**, 329.
18 K. Tomke, *Z. Phys. Chem., N.F*, 1977, **106**, 225.
19 K. Tanabe, *Catal. Today*, 1990, **8**, 1.
20 H. Ponceblanc, Ph.D. Thesis, University of Lyon, France, 1990, no. 172-90.
21 T. Yashima, H. Suzuki and N. Hara, *J. Catal.*, 1973, **30**, 362.
22 K. T. Seo, S. C. Kang, H. J. Kim and S. K. Moon, *Korean J. Chem. Eng.*, 1985, **2**, 163.
23 L. T. We and B. Delmon, *Appl. Catal. A*, 1992, **81**, 141.
24 J. M. M. Millet, H. Ponceblanc, G. Coudurier, J. M. Herrmann and J. C. Védrine, *J. Catal.*, 1993, in the press.
25 H. Ponceblanc, J. M. M. Millet, G. Coudurier and J. C. Védrine, *ACS Symp. Ser.*, 1993, **523**, 262.

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