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Study of Multiphasic Molybdate-Based Catalysts

I. Electrical Conductivity Study of Valence States and Solubility Limits in Mixed Iron and Cobalt Molybdates

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The electrical conductivity of a series of iron–cobalt molybdates has been measured at 370°C, as a function of the iron content. An important increase of the electrical conductivity occurred when small amounts of iron were substituted for cobalt. This takes place because iron is partially in the 3+ oxidation state. This species, which is stabilized into the $CoMoO_4$ structure, creates a valence induction effect which is responsible for the drastic variation of the electrical conductivity with compounds whose iron content ranges from 0 to 20%. UV spectroscopy allows us to propose that the ferric species involved in this valence induction phenomenon are those giving rise to the intervalence charge transfer between iron cations (Fe^{2+}–O–Fe^{3+}). By contrast, ESR spectroscopy is silent for such a phenomenon (too short relaxation time) and shows two typical Fe^{3+} (d^5 ion) spectra for Fe^{3+} engaged either in a different manner in the solid solution (strongly distorted octahedral site) or a given compound such as $Fe_2(MoO_4)_3$ observed at high iron content.

INTRODUCTION

It has been shown that the catalytic properties of molybdate-based catalysts can be improved by various additives, such as iron or cobalt (*1*) which are frequently used, especially in industrial catalysts. However, the exact nature of their insertion in the host lattice and their influence upon the other cations are not definitively established. Recently, temperature-programmed electrical conductivity measurements have been carried out on a series of mixed iron and cobalt molybdate catalysts in order to determine the influence of the iron cations and of their valence states on the solid–solid phase equilibria in the system $CoMoO_4$–$FeMoO_4$ (*2*). We have undertaken the study of the electrical conductivity as a function of the temperature and especially as a function of the iron content of the compounds.

In what follows, electrical conductivity measurements have been carried out on a series of mixed iron and cobalt molybdates with the general formula $Co_{1-x}Fe_xMoO_4$ ($0 \leq x \leq 1$) in order to study the influence of the iron cations on the electronic properties of the solids and to determine their valence state.

EXPERIMENTAL

1. SAMPLE PREPARATION

Mixed cobalt and iron molybdates were prepared by coprecipitation from cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$, ferrous chloride $FeCl_2 \cdot 4H_2O$, and ammonium heptamolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ mixtures, under controlled atmosphere, as previously described in (*2*).

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Precursors were then calcined at 500°C for 10 h under pure nitrogen flow. The low-temperature α-phase of these mixed molybdates was then obtained by grinding. In certain cases, the presence of Fe^{3+} has been decreased by treatment of the solids under a reducing gas flow (H_2/N_2 : 1/4; total flow rate = 5 $dm^3\ h^{-1}$) at 400°C (*2*) for times varying from 30 to 180 min. The determination of the Fe^{2+} and Fe^{3+} content by Mössbauer spectroscopy has been described in a previous paper (*2*).

2. ELECTRICAL CONDUCTIVITY MEASUREMENTS (EC)

The electrical conductivity (EC) of the samples was measured in a static cell previously described (*3*). An amount of 450 mg of the powder sample was placed between the two platinum electrodes under a constant mechanical pressure of 10^5 Pa. A dynamic vacuum of 8 Pa was established and maintained during all the experiments. The temperature of both electrodes was measured by two soldered thermocouples whose wires were also used as conductors for electrical measurements. The electrical resistance of the samples was measured, according to the range investigated, with a Kontron multimeter (model DMM 4021) or with a digital teraohmmeter (Guildline Instruments, model 9520), while temperature was increased at a rate of 5°C min^{-1} (*4*).

The samples behaved as bulk conductors and the apparent electrical conductivity σ ($\Omega^{-1}\ cm^{-1}$) was calculated from the conductance $1/R$ by taking into account the geometric factor t/S, in which t is the thickness of the compressed powder (about 0.5 cm) and S the section area of the electrodes (diameter 1 cm):

$$\sigma = (1/R) \cdot (t/S).$$

More accurate values of the electrical conductivity could be obtained by using the apparent volumic weight μ, and the mass of the sample m:

$$\sigma = (1/R) \cdot (1/S^2) \cdot m/\mu.$$

Electrical conductivity was previously used to determine the temperature of transition of various cobalt–iron molybdates under study (*2*). In the present case, this technique has been employed to follow the influence of the total iron content as well as the partial Fe^{3+} content upon solubility limits. For a better comparison between catalysts, the electrical conductivity of the different solids were measured in the same conditions, i.e., at the same temperature (370°C) using the same mass (ca. 450 mg), the same compression of the powder, and the same heating rate. The temperature of 370°C has been chosen for all the catalysts since it corresponds to the upper limit before the temperature of phase transition, which varies according to the phase composition of $Fe_xCo_{1-x}MoO_4$ solids.

3. ESR MEASUREMENTS

The ESR data were obtained using a Varian E 101 spectrometer equipped with a dual cavity. Measurements were performed at room or liquid nitrogen temperatures with a DPPH sample (g = 2.0036) for g value calibration.

4. UV MEASUREMENTS

UV spectra were recorded with a Perkin–Elmer spectrophotometer lambda-9 from 2500 to 185 nm with a diffuse reflectance attachment using $BaSO_4$ as a reference.

RESULTS AND DISCUSSION

1. ELECTRICAL CONDUCTIVITY AS A FUNCTION OF TOTAL IRON CONTENT

The electrical conductivity of $Fe_xCo_{1-x}MoO_4$ solids has been found to increase abruptly as a function of iron content. The results are presented in Fig. 1 and listed in Table 1. The semilog plot of Fig. 1 indicates two straight lines above and below the value of 17% iron. For 0% ≤ [Fe] ≤ 17%, EC increases by four orders of magnitude and then increases more gently until reaching the high conductivity value of pure iron mo-

TABLE 1

Electrical Conductivity Values at 370°C, and Apparent Activation Energies of Conduction of Mixed Iron and Cobalt Molybdates as a Function of Fe^{2+} and Fe^{3+} Contents ($Fe_t = Fe^{3+} + Fe^{2+}$)

Sample	$\frac{Fe_t}{Fe_t + Co}$	$\frac{Fe^{3+}}{Fe_t + Co}$	σ 370°C ($10^{-5}\ \Omega^{-1}\ cm^{-1}$)	E_c (kJ mol^{-1})
$CoMoO_4$	0	0	0.0022	142
CFM1	0.06	0.004	0.053	59
CFM2	0.11	0.014	4.60	46
		0.025	3.30	50
		0.037	2.75	54
CFM3	0.12	0.005	0.90	50
		0.026	2.40	42
CFM4	0.17	0.015	11.20	42
		0.021	12.60	42
		0.080	7.20	54
		0.093	4.00	54
CFM5	0.23	0.053	15.90	43
		0.080	16.40	67
CFM6	0.25	0.039	14.00	50
		0.075	11.50	54
CFM7	0.53	0.180	116.0	42
		0.254	62.00	75
CFM8	0.67	0.110	95.00	43
CFM9	0.86	0.063	520.0	54
$FeMoO_4$	1.00	0.070	520.0	54
$Fe_2Mo_3O_{12}$	1.00	1.00	40.00	45

lybdate $FeMoO_4$. The high increase of EC between zero and 17 at.% [Fe] can only be accounted for by a doping effect of cobalt molybdate $CoMoO_4$ by heterovalent iron ions according to the valence induction law.

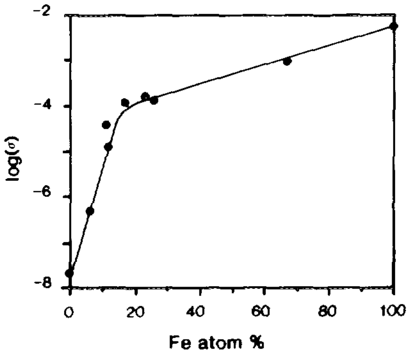

Fig. 1. Variation of the logarithm of electrical conductivity of mixed iron and cobalt molybdates as a function of total iron content.

This is discussed in subsection 2. The change of slope for [Fe] = 17 at.% clearly shows an Fe^{3+} solubility limit as previously observed in the case of mixed tin–antimony oxides (*5*). This solubility limit can be associated with the appearance of an ESR spectrum for [Fe] ≥ 20%, which has been ascribed to the detection of a stable Fe^{3+} species in the solid solution at higher iron content to the detection of ferric molybdate $Fe_2(MoO_4)_3$ phase (see subsection 2) whose existence has also been confirmed by XRD (*2*).

2. ELECTRICAL CONDUCTIVITY AS A FUNCTION OF FERRIC IRON CONTENT

2.1. Unreduced Mixed Iron and Cobalt Molybdates

As mentioned above, the steep increase of four orders of magnitude when the total atomic percentage of iron increases from zero to 17% can only be accounted for by a doping effect of $CoMoO_4$ by ferric ions dissolved in substitutional positions. The presence of Fe^{3+} has been detected in all the samples by chemical analysis and Mössbauer spectroscopy (*6*). According to the valence induction law, the dissolution of ferric ions Fe^{3+} by substitution of Co^{2+} in divalent lattice sites creates donor centers $[-(Fe^{3+})-e^-]$ represented by the symbol D. Iron can only share two electrons with two oxygens neighbours and, since its valence state is equal to 3+, an excess electron is generated by this controlled doping center. Only a very small energy is necessary to make this electron moves into the conduction band. The ionization can be written

$$[(-Fe^{3+}-)e^-] \rightarrow [(-Fe^{3+}-)\ldots] + e^-,$$

or more simply

$$D \rightarrow D^+ + e^-, \qquad (1)$$

where D represents a filled electron donor center and D^+ is the corresponding ionized donor center. The sum of their concentrations is equal to $[D_0]$, the nominal content of the heterocations introduced:

$$[D] + [D^+] = [D_0]. \qquad (2)$$

Moreover, the electroneutrality of the solid requires

$$[e^-] = [D^+]. \qquad (3)$$

Taking into account Eqs. (2) and (3), the mass action law applied to Eq. (1) yields

$$K = \frac{[D^+][e^-]}{[D]} = \frac{[D^+][e^-]}{[D_0] - [D^+]} = \frac{[e^-]^2}{[D_0] - [e^-]}. \qquad (4)$$

The general solution of Eq. (4) is given by

$$[e^-] = \frac{K}{2}\left[\left(1 + \frac{4[D_0]}{K}\right)^{1/2} - 1\right]. \qquad (5)$$

This general equation exhibits two limit cases.

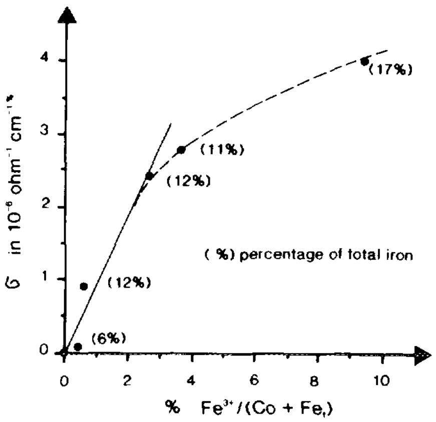

FIG. 2. Variation of electrical conductivity of mixed iron and cobalt molybdates as a function of Fe^{3+} content (samples were not reduced under H_2).

Case 1: $4[D_0]/K \ll 1$. This corresponds to an almost total ionization of the donor centers with a relatively low total concentration of donor centers (a few atom percent). In Eq. (5), the condition simplifies the radical with a limited development:

$$\left(1 + \frac{4[D_0]}{K}\right)^{1/2} \cong 1 + \frac{2[D_0]}{K}. \qquad (6)$$

Consequently, Eq. (5) becomes

$$[e^-] \cong \frac{K}{2}\left(1 + \frac{2[D_0]}{K} - 1\right) \cong [D_0]. \qquad (7)$$

This means that each heterovalent ion introduced in the lattice of the host oxide produced one free electron of conduction. In other words, from Eqs. (2) and (3), one gets $[D_0] \cong [D^+] = [e^-]$.

This is experimentally observed by plotting σ as a function of $[Fe^{3+}]$ determined for each sample by chemical analysis (Fig. 2). The linear variations of $\sigma = f(Fe^{3+})$ for $0\% \leq Fe^{3+} \leq 3\%$ indicates unambiguously that all the Fe^{3+} ions introduced in the system are dissolved in divalent sites liberating one free electron per atom.

Case 2: $4[D_0]/K \gg 1$. This case corresponds to a high total concentration in donor centers. The general solution (Eq. (5)) becomes equal to

$$[e^-] \cong \frac{K}{2}\left(\frac{4[D_0]}{K}\right)^{1/2} = (K[D_0])^{1/2}. \qquad (8)$$

The concentration in free electrons is no more proportional to $[D_0]$ but to its square root. This is observed for $[Fe^{3+}] \geq 3\%$ (Fig. 2), where σ no longer varies proportionally to $[Fe^{3+}]$.

2.2. *Reduced Mixed Iron and Cobalt Molybdates*

For a same total iron content, the percentage of Fe^{3+} has been modified by reducing the solids in hydrogen. For the same solid, EC should decrease when $[Fe^{3+}]$ is decreased by reduction. In fact, the observed behaviour was the opposite (see, for instance, CFM2, CFM4, CFM6 and CFM7 in Table 1). This appears to be in contradiction with the valence induction law described above. Actually, these unexpected variations can be easily explained if one considers that EC reflects two simultaneous phenomena:

— a decrease of the doping effect due to the reduction by H_2 of Fe^{3+} into Fe^{2+} which is isoelectronic to Co^{2+};

— an increase of the free electron concentration originating from the creation of ionized anionic vacancies. Hydrogen not only reduces Fe^{3+} into Fe^{2+} but also the oxygen surface lattice of the molybdic phase. This creates anionic vacancies according to the reaction

$$O_S^{2-} + H_2 \rightarrow H_2O + V_{O^{2-}}, \qquad (9)$$

where O_S^{2-} represents a surface lattice anion and $V_{O^{2-}}$ is an anionic vacancy with two trapped electrons (neutral entity with respect to the lattice). This anionic vacancy can spontaneously become ionized by loosing its first electron according to the equation

$$V_{O^{2-}} \rightarrow V_{O^{2-}}^{+} + e^-. \qquad (10)$$

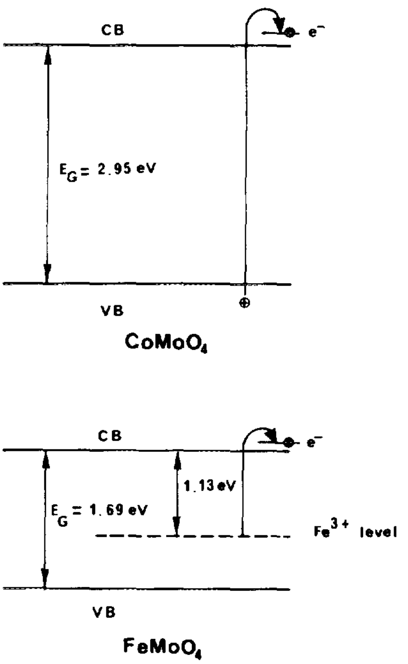

FIG. 3. Energy band diagram of cobalt and iron molybdates.

In the present case, the electrons generated in Eq. (10) are more numerous than those consumed by the reduction of Fe^{3+} into Fe^{2+}, which explains why EC increases although $[Fe^{3+}]$ apparently decreases.

2.3. *Electrical Conductivity of Pure Cobalt and Iron Molybdates*

2.3.1. $CoMoO_4$. This pure phase has the lowest EC value at 370°C ($\sigma = 2.2.10^{-8}$ $ohm^{-1} \cdot cm^{-1}$) and the highest activation energy of conduction ($E_C = 142$ kJ mol^{-1}) (see Table 1). Pure $CoMoO_4$ can be considered as an intrinsic semiconductor in the absence of impurities (dopes) or of a reduced state. In that case, conduction electrons arise from the promotion from the valence band into the conduction band (Fig. 3) and the theory shows that the energy band gap is equal to twice the activation energy of conduction $E_G = 2E_C = 2.95$ eV. An absorption threshold at $\lambda = 420$ nm should correspond to this band gap energy. This value is in excellent agreement with the value obtained for β-$CoMoO_4$ in the UV–visible spectrum of Fig. 4.

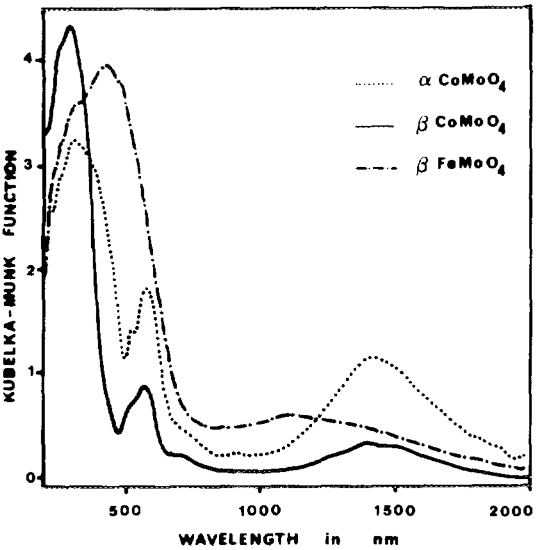

FIG. 4. UV–visible spectra of α-$CoMoO_4$, β-$CoMoO_4$, and α-$FeMoO_4$.

2.3.2. $FeMoO_4$. From the results of Table 1, iron molybdate appears with a very high EC value measured at 370°C and, correspondly, with a rather low activation energy of conduction, in contrast with the undoped $CoMoO_4$. $FeMoO_4$ cannot be considered an intrinsic semiconductor as its cobalt homologue. From the UV–visible spectrum in Fig. 4, one can deduce a band gap energy E_G equal to 1.69 eV from the formula $E_G(eV) = 1.24\ 10^{-3}/\lambda(nm)$. This value (1.69 eV) is quite different from that of the double of the activation energy of conduction from ($2E_C = 1.12$ eV). Consequently, pure $FeMoO_4$ phase is an extrinsic semiconductor whose band gap is close to 1.7 eV and which possesses an impurity level located, according to the theory, at a distance ε equal to $2E_C$, below the conduction band level, i.e., 1.12 eV (see Fig. 3). A wavelength equal to 1105 nm corresponds to this energy level. Actually, a band at 1114 nm appears in the UV–visible spectrum (Fig. 4). The extrinsic semiconductor nature of $FeMoO_4$ can be associated with the existence of impurities acting as donor centers. Since $FeMoO_4$ was tentatively prepared as a pure phase, the impurities can only originate from the system itself. In other words, impurities are due to Fe^{3+} ions, which are spontaneously formed because of the favorable Fe^{3+}/Fe^{2+} redox potential, although pure ferrous $FeMoO_4$ molybdate was the final product desired. The existence of Fe^{3+} in $FeMoO_4$ has been shown by chemical analysis (see Table 1) and Mössbauer spectroscopy (*6*). In the present case, EC indicates that Fe^{3+} ions are dissolved in $FeMoO_4$. The strong doping effect of Fe^{3+} in ferrous molybdate accounts for the small EC of $FeMoO_4$ in comparison with that of pure $CoMoO_4$ (Table 1). It can be observed from the electrical conductivity study that it is impossible to obtain a pure ferrous phase by the method of preparation used, since always ferric ions are present.

3. ELECTRON SPIN RESONANCE SPECTROSCOPY

The samples have also been characterized by ESR. For samples with a total iron content below 20%, no signal was detected, although chemical analysis and Mössbauer spectroscopy show that they contain Fe^{3+}. This phenomenon can be explained by a delocalisation of the free electron associated to Fe^{3+} within the whole material.

For samples with a total iron content between 20 and 25%, and 25 and 100%, a weak and broad signal ($g = 2.30$) and a symmetrical and intense signal were respectively observed. These signals can be attributed in the first case to Fe^{3+} in a strongly distorted octahedral site, presumably in the solid solution (the ferric cations would in this case likely be locally balanced with cations vacancies) and, in the second case, to Fe^{3+} in the $Fe_2Mo_3O_{12}$ structure.

In other words, the nonobservable free electron (not observable because of a too fast relaxation time) is related to electrical conductivity. At variance, the intense ESR spectrum of Fe^{3+} corresponds to Fe^{3+} in defined crystallographic phases.

4. UV–VISIBLE SPECTROSCOPY

The UV spectra of the samples were composed of the characteristic bands of the Fe^{2+}

and Co^{2+} ions in octahedral symmetry and of intense charge transfer absorptions. For iron contents less than 30%, the absorptions at 6900–7410, 17,390, and 18,520 cm^{-1} correspond mainly to the d–d transitions of Co^{2+} (d^7), ($^4T_{1g}(F) \Rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \Rightarrow {}^4T_{1g}(P)$, respectively). The presence of Fe^{2+} (d^6) induces a broadening at 9090 cm^{-1} (transition $^5T_{2g}(D) \Rightarrow {}^5E_g(D)$). But the dominant feature was the appearance of an intense band near 22,200 cm^{-1} that increased with the iron content. This band surimposed to the charge transfer band $O^{2-} \Rightarrow Mo^{6+}$ observed at 33,300 cm^{-1} in pure $CoMoO_4$ (*7*).

For higher iron concentrations, only a weak and very broad band was observed in the visible range (6000 to 11,000 cm^{-1}) with two humps at 7200 and 8700 cm^{-1} in addition to the very intense charge transfer band at 22,200 cm^{-1}.

The later band is too intense to be ascribed to d–d transitions and corresponds to the surimposition of both an $O^{2-} \Rightarrow Mo^{6+}$ charge transfer (33,300 cm^{-1}) and an intervalence charge transfer $Fe^{2+} \Rightarrow Fe^{3+}$. The presence of such an electronic transfer implies the existence of O^{2-} ions bridging the two ions Fe^{2+} and Fe^{3+}. It may be suggested that the Fe^{3+} ions occupy the sites of Fe^{2+} in the chains of face-sharing octahedra of the molybdate structure. The electron associated to substituted Fe^{3+} is very probably responsible for the high electrical conductivity increase. This free electron is ESR silent probably because of a too short relaxation time.

The band at 22,200 cm^{-1} has been used to characterize iron ions in the molybdate phase. Figure 5 shows the variation of its intensity (calculated as the difference between the total intensity measured and the contribution of the $O^{2-} \Rightarrow Mo^{6+}$ charge transfer band which is taken to be proportional to the content in molybdenum) as a function of the iron content of the samples. The curve obtained is very similar to that of the variation of log σ (Fig. 2) with a strong increase in optical density between 0 to 20% iron. Thus, it is suggested that the Fe^{3+} species giving rise to the intervalence band transfer and not detectable by ESR are only those involved in the increase in electrical conductivity. It can be proposed that they should correspond to all the Fe^{3+} species chemically characterized in the samples with 0 to 20% iron. In the samples richer in iron the presence of additional Fe^{3+} species related to structural defects in the solid solution and to Fe^{3+} species in a well defined phase of ferric molybdate is detected by ESR.

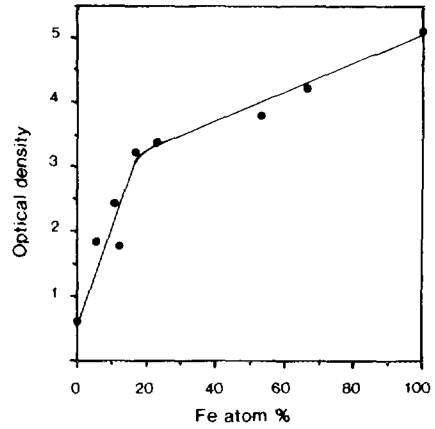

FIG. 5. Variation of the optical density of the band at 22,200 cm^{-1} as a function of the total iron content of the molybdates.

CONCLUSION

The study of mixed iron and cobalt molybdates showed that an important increase of the electrical conductivity occurred when small amounts of Fe^{3+} were substituted for Co^{2+}. This took place when iron was partially oxidized into Fe^{3+} which was stabilized into the $CoMoO_4$ structure and induced a valence induction effect responsible for the drastic variation of the electrical conductivity and for an intervalence charge transfer. These ferric ions are always present even in phases where ferrous species were exclusively desired. At high iron content, other Fe^{3+} species engaged in the solid solution or in a given compound such as $Fe_2(MoO_4)_3$ are observed.

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